

PHENYL AND NITROPHENYL TITANATES

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Titanates of some di- and trihydroxyphenols and mono-, di- and trinitrophenols have been prepared by the action of titanic bromide on these phenols and nitrophenols, and their properties studied. The organic components of the titanates have been estimated potentiometrically by the excess bromination method.

Levy (*Ann. chim. phys.*, 1893, *vi*, 28, 433) prepared phenyl, *m*- and *p*-cresyl, thymyl and α -naphthyl titanates by the action of TiCl_4 on the corresponding phenol in benzene solution and studied their properties. He obtained a brick-red substance of the composition $2\text{TiCl}_4 \cdot \text{Ti}[\text{O} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3]_4$ by treating TiCl_4 with picric acid in benzene solution, which on prolonged boiling in the solvent gave picryl titanate $\text{Ti}[\text{O} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3]_4$.

Rosenheim and Sorge (*Ber.*, 1920, 53, 932) and Rosenheim *et al.* (*Z. anorg. Chem.*, 1931, 196, 160) prepared titanates of catechol by dissolving titanic acid in alkaline solution of catechol having the composition $\text{M}_x[\text{Ti}(\text{C}_6\text{H}_4\text{O}_2)_2] \cdot x\text{H}_2\text{O}$ (where x is usually 1). Besides, photometric studies of hydroquinone and pyrogallol acid complexes of titanium were carried out by Ikenberry *et al.* (*Anal. Chem.*, 1953, 25, 1340) and absorption spectra for these complexes were given in the near ultraviolet and visible regions.

The present communication deals with a systematic study of the titanates formed by the action of some di- and trihydroxyphenols and mono-, di- and trinitrophenols on titanic bromide.

EXPERIMENTAL

The chemicals used were of Merck or B.D.H. 'extra pure' quality. The phenols or nitrophenols were recrystallised before use. Titanium tetrabromide was prepared by the method of Olsen and Ryan (*J. Amer. Chem. Soc.*, 1932, 54, 2215), redistilled at 230° and extracted with anhydrous ether.

General Procedure.—Ethereal solutions of TiBr_4 and phenol or nitrophenol were mixed together and the mixture slowly warmed at about $50\text{--}60^\circ$ on an oil-bath for about half an hour. The temperature of the bath was then slowly raised and finally the residue was heated at a temperature slightly higher ($10\text{--}15^\circ$) than the m.p. of the corresponding phenol or nitrophenol till HBr had ceased to evolve. It was observed that the reaction started even at the ordinary temperature with the evolution of HBr and became more vigorous with the rise in temperature. The mass was taken out, washed well with anhydrous ether, dried at about $40\text{--}45^\circ$, analysed and its properties studied.

As phenolphthalein is insoluble in ether, its reaction with TiBr_4 was carried out in alcoholic medium. In this case the reaction was slow as compared with

other titanates, and complete only when the mixture was heated at 260-70° for about 4 hours. The reaction product was washed well with alcohol and analysed.

Estimation.—The phenols or nitrophenols of the corresponding phenyl or nitrophenyl titanates were estimated potentiometrically by the excess bromination method, but the method was not successful in the case of compounds formed with pyrogallol, phenolphthalein, 2:4-dinitro-*z*-naphthol and picric acid. Hence, in these titanates carbon and hydrogen were estimated by combustion method, nitrogen by the Dumas method and titanium, as TiO_2 .

Estimation of Phenols and Nitrophenols.—The compound was weighed out accurately (about 0.1–0.7 g.) and treated with a warm 2*N* solution of NaOH, filtered and the residue $Ti(OH)_4$ washed well with hot water. The filtrate and the washings were collected and the volume made up to 250 c.c. The solution (25 c.c.) was pipetted out in an iodine flask and 15 c.c. of each solution, 4*N*-HCl, *M*/2-KBr and 0.1*N*- $KBrO_3$ were added to it and the mixture kept for about half an hour with frequent shaking. 0.1*N*- As_2O_3 (15 c.c.) was then added to it and filtered in case any turbidity or precipitate appeared. It was transferred to the titrating vessel and titrated with 0.1*N*- $KBrO_3$. From the amount of bromine consumed, the quantity of phenol or nitrophenol present in the compound was calculated. The results are recorded in Table I.

As some of the phenols or nitrophenols used formed mono-, di-, tri- and even tetra-bromo derivatives, a blank titration was carried out in each case. The quantities of bromine consumed by them are also shown in Table I.

TABLE I

[T denotes titanate]

Compounds taken.	Wt. of the phenol or nitrophenol available.	Bromine consumed per mole of the phenol or nitrophenol.		
		Calc.	Found.	
Phloroglucinol,	0.1230 g.	0.1230 g.	0.1228 g.	3 Br ₂
<i>o</i> -Nitrophenol,	0.2876	0.2876	0.2876	2 Br ₂
Resorcin-T,	0.1246	0.1038	0.1032	3 Br ₂
Catechol-T,	0.1510	0.1258	0.1255	4 Br ₂
Phloroglucinol-T,	0.0908	0.0773	0.0768	3 Br ₂
Hydroquinone-T,	0.2024	0.1687	0.1690	1 Br ₂
<i>o</i> -Nitrophenyl-T,	0.2098	0.1944	0.1936	2 Br ₂
<i>m</i> -Nitrophenyl-T,	0.1676	0.1551	0.1558	3 Br ₂
<i>p</i> -Nitrophenyl-T,	0.2738	0.2537	0.2526	2 Br ₂
2:4-Dinitrophenyl-T,	0.6824	0.6488	0.6463	1 Br ₂

TABLE II

Phenols.	Mol. formula of corresp. titanate.	Colour.	% Titanium.		% Carbon.		% Hydrogen.	
			Found.	Calc.	Found.	Calc.	Found.	Calc.
Resorcinol	Ti(C ₆ H ₄ O ₂) ₂	Black	18.12	18.18	54.25	54.55	3.01	3.03
Catechol	Ti(C ₆ H ₄ O ₂) ₂	Deep brown	18.10	18.18	54.46	54.55	3.02	3.03
Pyrogallol	Ti(C ₆ H ₃ O ₂ .OH) ₂	Brownish black	16.15	16.22	48.46	48.65	2.68	2.70
Hydroquinone	Ti(C ₆ H ₄ O ₂) ₂	Chocolate brown	18.21	18.18	54.67	54.55	3.04	3.03
Phloroglucinol	Ti(C ₆ H ₃ O ₂ .OH) ₂	Deep reddish brown	16.20	16.22	48.41	48.65	2.69	2.70
Phenolphthalein	Ti(C ₁₀ H ₂₄ O ₈) ₂	Shining black	7.03	7.06	70.16	70.59	3.44	2.53

TABLE III

Nitro-phenols.	Mol. formula of corresp. titanate.	Colour.	M.P.	% Titanium.		% Carbon.		% Hydrogen.		% Nitrogen.	
				Found.	Calc.	Found.	Calc.	Found.	Calc.	Found.	Calc.
<i>o</i> -Nitro-	Ti(NO ₂ .C ₆ H ₄ O) ₄	Shining black	...	7.98	8.00	23.89	24.00	2.65	2.67	9.29	9.33
<i>m</i> -Nitro-	Ti(NO ₂ .C ₆ H ₄ O) ₄	Greyish black	...	7.96	8.00	24.10	24.00	2.68	2.67	9.37	9.33
<i>p</i> -Nitro-	Ti(NO ₂ .C ₆ H ₄ O) ₄	Greyish black	97°	7.96	8.00	23.90	24.00	2.66	2.67	9.29	9.33
2:4-Dinitro-	Ti[(NO ₂) ₂ C ₆ H ₃ O] ₄	Greyish brown	110.6°	6.17	6.15	37.07	36.92	1.55	1.54	14.42	14.36
Picric-acid.	Ti[(NO ₂) ₃ C ₆ H ₃ O] ₄	Deep dark brown	152°	4.98	5.00	30.21	30.00	0.82	0.83	17.38	17.50
2:4-Dinitro- <i>a</i> -naphthol.	Ti[(NO ₂) ₂ C ₁₀ H ₆ O] ₄	Pitch- black	122°	4.91	4.90	48.62	48.98	2.02	2.04	11.37	11.43

DISCUSSION

All the compounds formed with phenols and titanium tetrabromide are very stable and insoluble in common organic solvents except those formed with resorcinol and phloroglucinol, which are sparingly soluble in alcohol and begin to hydrolyse even at the room temperature. All these titanates are slightly soluble in dilute mineral acids but readily in HNO₃(conc.) or aqua regia except phenolphthalein titanate, which is insoluble even in concentrated acids. They hydrolyse slowly with water and alcohol, but readily with alkalis, and Ti(OH)₄ is precipitated. The reaction with trihydroxy-

phenol is more vigorous and is over in shorter duration. On analysis it has been found that only two hydroxyl groups take part in the reaction. In absence of the requisite data to fix the position of free (OH) group, no definite structural formulae can be assigned to the compounds formed with $TiBr_4$ and trihydroxyphenols.

The compounds formed with mono-, di- or trinitrophenols are similar to those formed with phenols, but these are insoluble in ether, petroleum ether, carbon tetrachloride and benzene. Unlike the compounds formed with di- or trihydroxyphenols, some of the nitrophenyl titanates give sharp m.p. (vide Table III). The analysis of these compounds indicates that four molecules of nitrophenols react with one molecule of $TiBr_4$ to give the corresponding nitrophenyl titanate and may be represented like the phenyl titanates, prepared by Levy (*loc. cit.*).

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