The Bond Refraction Values for Ti-O in Organic Titanates

By Tooru TAKATANI

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Many liquid organic titanates are known, but little attention has been paid to the calculation of the molecular refraction values of these compounds.

English and Sommer[1] have recently obtained tetrakis-(trimethylsiloxy)-titane, and have measured its molecular refraction, estimating the bond refraction for Ti-O as 4.02 ml./mol. This seems to be the only example which has appeared in the literature published so far.

For the present paper, the establishment of bond refraction for Ti-O and its application for some organic titanates were undertaken.

Experiment

Ethyl, iso-propyl, and n-butyl titanate were prepared by treating titanium tetrachloride with corresponding alcohol in the presence of ammonia[2].

n-Propyl, sec-butyl, tert-butyl, and tert-pentyl titanate were prepared by the transesterification reaction (1) between ethyl titanate and the corresponding alcohol[3].

$$(C_2H_5O)_4Ti + 4\ ROH = (RO)_4Ti + 4\ C_2H_5OH \quad (1)$$

The preparation of *n-Heptyl titanate* followed a similar method, n-butyl titanate being used in place of ethyl titanate.

Some of the physical properties and titanium contents of the titanates prepared are shown in Table I and II.

Ethyl Titanate.—Ethanol (460 g, 10 mol.) was saturated with ammonia in a flask fitted with a reflux condenser, and all openings were protected against moisture. Titanium tetrachloride (190 g, 1 mol.) was then added drop by drop while

1) W. D. English and L. H. Sommer, *J. Am. Chem. Soc.*, **77**, 170 (1955).

2) J. Nelles, U. S. Patent 2,187,821 (1940), *Chem. Abst.*, **34**, 3764[7] (1940).

3) B. A. Arbuzov and Z. G. Isaeva, *Zhur. Obshchei Khim.* S. S. S. R., **22**, 566 (1952), *Chem. Abst.*, **47**, 2684 f (1953).

stirring under cooling by ice during five hours at a temperature below 60°C. After the addition, the mixture was allowed to stand overnight at room temperature. White precipitates of ammonium chloride were removed and the filtrate was heated on a water bath to eliminate the excess of ethanol. The residue was distilled under reduced pressure, to obtain a fraction b.p. 140–145°C/3mmHg (reported, 130–132°C/2mmHg[4]). It was redistilled and used for further experiments.

Anal. Found: Ti, 21.1; C_2H_5O, 79.3. Calcd. for $(C_2H_5O)_4Ti$: Ti, 21.0; C_2H_5O, 79.0 %.

Titanium was determined by the Speer's method[5] and the ethoxy group by Bradley's oxidation method[6].

TABLE I
PROPERTIES AND ANALYSES OF THE PREPARED TITANATES

Compd.	B.P. °C/mmHg	M.P. °C	Ti Found	Ti Calcd.
(*n*-$C_3H_7O)_4Ti$	137–40/3a)		16.9%	17.0%
(*iso*-$C_3H_7O)_4Ti$	97– 8/8	15	16.8	17.0
(*sec*-$C_4H_9O)_4Ti$	107– 9/3b)		14.2	14.1
(*tert*-$C_4H_9O)_4Ti$	85– 7/3c)		14.2	14.1
(*n*-$C_5H_{11}O)_4Ti$	182– 3/3d)		12.3	12.1
(*tert*-$C_5H_{11}O)_4Ti$	129–30/2e)		12.2	12.1
$(C_6H_{11}O)_4Ti$	220– 5/3f)	43	10.6	10.8
(*n*-$C_7H_{15}O)_4Ti$	215–20/1g)		9.47	9.42

a) 170/3[5], 171/14[7], b) 90–2/0.5–1[5], c) 62–3/1[5], 102/1[7], d) 175/0.8[8], 158/0.1[8], 211/11[7], e) 98/0.1[9], f) 1[0].5–2.0/1[10], g) 213/0.4[9], 201/0.1[9]264–5/15[11].

***n*-Propyl Titanate.**—A mixture of ethyl titanate (22.8 g, 0.1 mol.) and *n*-propanol 30.1 g, 0.5 mol.) was heated to remove the ethanol produced during the reaction. After the theoretical quantity of ethanol was recovered, the residue was distilled under reduced pressure. *n*-Propyl titanate was obtained in 75 % yield.

***tert*-Butyl Titanate.**—It was impossible to prepare this compound by reacting titanium tetrachloride with *tert*-butanol or sodium-*tert*-butoxide. The manipulation of the transesterification reaction between ethyl titanate and *tert*-butanol was somewhat complicated, because the separation of ethanol produced and *tert*-butanol by fractional distillation was difficult.

tert-Butyl titanate was obtained from ethyl titanate (22.8 g, 0.1 mol.) and *tert*-butanol (37.0 g, 0.5 mol.) following the method as in the case of *n*-propyl titanate. After ethanol and *tert*--butanol were distilled off, the residue was treated with *tert*-butanol (7. 4 g, 0.1 mol.). This procedure was repeated ten times to complete reaction, *tert*-butyl titanate being obtained by distillation under reduced pressure in 52 % yield.

Results and Discussion

There are eighteen sets of densities and refractive indices of organic titanates and chlorotitanates which were observed at the same temperature as shown in Table III. From these data, molecular refraction of each compound was calculated. The sum of Denbigh's bond refraction[15] for C–C, C–H, C–O was reduced from the molecular refraction of the compound, the remainder being divided by the number of Ti–O bonds in a molecule, and the bond refraction for Ti–O was obtained. As the bond refraction for Ti–Cl has not appeared in the literature, it was calculated, using

TABLE II
MOLECULAR REFRACTIONS OF THE PREPARED TITANATES

Compd.	Dens. d_4^t	Refr. Ind. n_D^t	Temp. °C	Mol. Refr. (ml./mol.) Obs.	Calcd.	Error
(*n*-$C_3H_7O)_4Ti$	1.0358a)	1.4907a)	35	79.41	79.68	−0.34%
(*iso*-$C_3H_7O)_4Ti$	0.9711	1.4678	20	81.34	79.68	+2.0
(*sec*-$C_4H_9O)_4Ti$	0.9463a)	1.4587a)	35	98.27	98.20	+0.07
(*tert*-$C_4H_9O)_4Ti$	0.8917a)	1.4368a)	20	99.96	98.20	+1.8
(*n*-$C_5H_{11}O)_4Ti$	0.9703	1.4813	35	116.34	116.56	−0.18
(*tert*-$C_5H_{11}O)_4Ti$	0.9118	1.4543	20	117.82	116.56	+1.1
$(C_6H_{11}O)_4Ti$	1.0589b)	1.5155b)	35	126.69	126.72	−0.12
(*n*-$C_7H_{15}O)_4Ti$	0.9430a)	1.4830a)	20	154.05	153.76	+0.20

a) Literature is shown in Table III.
b) Supercooled Liquid.

4) O. V. Nogina, and A. B. Belyavskii, *Akad. Nauk S. S. S. R., Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik*, **2**, 164 (1952), *Chem. Abst.*, **48**, 567 c (1954).
5) R. J. Speer, *J. Org. Chem.*, **14**, 655 (1949).
6) D. C. Bradley, F. M. Abd-el Halim and W. Wardlaw, *J. Chem. Soc.*, **1950**, 3450.
7) N. M. Cullinane, S. J, Chard, G. F. Price, B. B. Millward and G. Langlois, *J. Appl. Chem.*, **1**, 400 (1951).
8) D. C. Bradley, R. C. Mehrotra and W. Wardlaw, *J. Chem. Soc.*, **1952**, 2027.
9) D. C. Bradley, R. C. Mehrotra, J. D. Swanick and W. Wardlaw, ibid., **1953**, 2025.
10) O. A. Nogina, R. Kh. Freidlina and A. N. Nesmeyanov, *Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk*, **1950**, 32, *Chem. Abst.*, **44**, 8854 i (1950).
11) B. A Arbuzov and T. G. Shavsha, *Doklady Akad, Nauk S. S. S. R.*, **68**, 859 (1949), *Chem. Abst.*, **44**, 886 e (1950).

TABLE III

CALCULATED BOND REFRACTIONS FOR Ti-O FROM THE DATA IN LITERATURE

Compounds	Dens. d_4^t	Refr. Ind. n_D^t	Temp. °C	Bond Refr. for Ti-O ml./mol.	Lit.
$(C_2H_5O)_4Ti$	1.1071	1.5051	35	4.07	5)
$(n\text{-}C_3H_7O)_4Ti$	0.9970	1.4803	35	4.42a)	5)
$(n\text{-}C_4H_9O)_4Ti$	1.0051	1.4925	20	4.11	12)
$(n\text{-}C_4H_9O)_4Ti$	0.9927	1.4863	35	4.16	5)
$(sec\text{-}C_4H_9O)_4Ti$	0.9196	1.4550	35	4.63a)	5)
$(tert\text{-}C_4H_9O)_4Ti$	0.8893	1.4436	20	4.93a)	5)
$(n\text{-}C_6H_{13}O)_4Ti$	0.9573	1.4830	20	4.03	12)
$(n\text{-}C_7H_{15}O)_4Ti$	0.8963	1.4810	20	4.59a)	11)
$(n\text{-}C_8H_{17}O)_4Ti$	0.9339	1.4810	20	4.09	12)
$(n\text{-}C_9H_{19}O)_4Ti$	0.9241	1.4785	20	3.97	12)
$(CH_3OC_2H_4O)_4Ti$	1.1910	1.5077	18	4.17	13)
$(C_2H_5OC_2H_4O)_4Ti$	1.1106	1.4920	21	4.17	13)
$[(CH_3)_3SiO]_4Ti$	0.9078	1.4278	20	4.02	1)
$(n\text{-}C_4H_9O)_3TiCl$	1.0985	1.5169	20	4.16	14)
$(C_2H_5OC_2H_4O)_3TiCl$	1.2035	1.5178	20	4.03	14)
$(iso\text{-}C_4H_9O)_3TiCl$	1.1043	1.5158	20	3.97	14)
$(iso\text{-}C_5H_{11}O)_3TiCl$	1.0600	1.5092	20	4.13	14)
$(n\text{-}C_6H_{13}O)_3TiCl$	1.0039	1.5050	20	5.25a)	14)
				Mean 4.08	

a) Except for the calculation of the mean value.

the values of titanium tetrachloride, $d_4^{20.1}$ 1.7344 and $n_D^{20.1}$ 1.6085, obtaining 9.46 ml./mol.[16] This value was used throughout the present investigation.

Eighteen bond refraction values for Ti-O were thus obtained, but as five values among them were far apart from the other thirteen values, the mean value was taken for all except these five values. The average bond refraction for Ti-O was obtained as 4.08 ml./mol.

Then, *n*-propyl, *sec*-butyl, *tert*-butyl, *n*-heptyl, *iso*-propyl, *n*-pentyl, *tert*-pentyl and cyclohexyl titanate were prepared, purified, and their densities and refractive indices were measured. In the calculation of the mean value of bond refractions for Ti-O the first four titanates were excepted.

Densities and refractive indices measured at the same temperature of the last four titanates have not been reported in the literature.

Molecular refractions obtained from these data of the titanates prepared were compared with the calculated ones using the bond refraction for Ti-O, 4.08 ml./mol. Both were in good agreement except for *iso*-propyl, *tert*-butyl, and *tert*-pentyl titanate. Thus the value 4.08 ml./mol. for Ti-O, was justified by these considerations.

The errors of molecular refractions of *iso*-propyl, *tert*-butyl, and *tert*-pentyl titanate amount to +2.0, +1.8, +1.1 %, respectively. According to Denbigh, the observed molecular refractions of many compounds agree with the calculated ones in a range of ±0.7 % error.

Considering this fact, the observed molecular refractions of these three titanates seem to be considarably large. The purity of these titanates was sufficient, viewed from their titanium contents. Particularly, *iso*-propyl titanate was obtained in a crystalline form by leaving the liquid standing for a long time. The cause of the observed greater molecular refractions of these titanates may be attributed to their greater hygroscopicity. Actually, refractive indices of these compounds gradually change greater during the measurement using Abbe's refractometer.

In the course of the preparation of *tert*-butyl and *tert*-butyl titanate, an interesting fact was observed. It has been indicated by us[17] that the transesterification reaction between ethyl silicate and *tert*-butanol

12) B. A. Arbuzov and T. G. Lsaeva, *Zhur. Obshchei Khim. S. S. S. R.*, **22**, 566 (1952), *Chem. Abst.*, **47**, 2684 g (1953).

13) A. N. Nesmeyanov, R. Kh. Freidlina and O. V. Nogina, *Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk*, **1951**, 518, *Chem. Abst.*, **46**, 7038 i (1952).

14) O. V. Nogina, R. Kh. Freidlina and A. N. Nesmeyanov, *Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk*, **1952**, 74, *Chem. Abst.*, **47**, 1583 f (1953).

15) K. G. Denbigh, *Trans. Farad. Soc.*, **36**, 936 (1940).

16) "Landolt-Börnstein Physiknlisch-Chemischen Tabellen". 5 Aufl. Zweiter Frgänzba. Zweiter Teil. Verlag von, Julius Springer Berlin (1931), S. 815.

17) Presented at the Annual Meeting of the Chem. Soc. of Japan in 1955.

or *tert*-pentanol proceeds incompletely as shown in the following equation (2)

$$(C_2H_5O)_4Si + 2\,tert\text{-}C_4H_9OH = (C_2H_5O)_2(tert\text{-}C_4H_9O)_2Si + 2\,C_2H_5OH. \quad (2)$$

However, when ethyl titanate was used in place of ethyl silicate, the transesterification reaction proceeded almost completely, and the titanates tetrasubstituted by *tert*-alkyl groups were obtained. It seems that titanium, the central metallic atom of the titanate, is large enough to diminish the steric effect of *tert*-alkoxy groups, which caused the incomplete transesterification reaction in the case of silicium.

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Hitachi Central Research Laboratory
Kokubunji, Tokyo