bp 63–64° (8 mm) [lit., bp[54] 191 °(760 mm)] was obtained. The pmr spectrum verified the structure.

trans-**Chloro(2-isopropylphenyl)bis(triethylphosphine)nickel(II).** The compound was prepared from the Grignard reagent of 2-chloroisopropylbenzene (17 mmol) and 3.65 g (10 mmol) of *trans*-dichlorobis(triethylphosphine)nickel(II) in tetrahydrofuran, using the same procedure as for the synthesis of **3a**. Recrystallization from hexane of the material obtained in the hexane trituration step afforded 3.20 g (70%) of crude product. A portion of this, 0.76 g, was chromatographed on acid-washed alumina under nitrogen. Recrystallization from hexane of material afforded by elution with 1:4 ether–hexane gave 0.65 g of golden brown crystals, mp 121–122°.

Anal. Calcd for $C_{21}H_{41}ClNiP_2$: C, 56.09; H, 9.19. Found: C, 56.05; H, 9.13. The pmr spectrum (C_6D_6) exhibited aromatic proton multiplets at τ 2.62 and 3.13, a single doublet at τ 8.64 attributed to the isopropyl substituent CH_3 protons, and two Et_3P proton multiplets near τ 8.77 and 8.99. The "benzylic" proton resonance (Table III) consisted of a septet with line separations identical with those in isopropylbenzene.

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the University of North Dakota grant-in-aid program for support of this research. We are grateful to the National Science Foundation for a departmental equipment grant, No. GP-8280.

---

(54) R. R. Dreisbach and R. A. Martin, *Ind. Eng. Chem.*, **41**, 2875 (1949).

A Structural Study of Titanium Tetraethoxide in Solution

W. R. Russo and W. H. Nelson

Department of Chemistry, University of Rhode Island,
Kingston, Rhode Island 02881. Received July 7, 1969

Abstract: A special light-scattering photometer equipped with a He–Ne CW laser source has been used for the precise measurement of the anisotropic Rayleigh scattering needed to calculate the optical anisotropy of titanium tetraethoxide in cyclohexane and carbon tetrachloride solutions. Turbidity measurements have confirmed the existence of a trimer unit in solution. The anisotropy values of likely titanium ethoxide structures have been calculated using a Δ-function model to obtain bond polarizabilities. Comparison of calculated and experimentally determined anisotropy values has indicated that the structure in solution consists of three polyhedra sharing edges, with the central titanium atom being six-coordinate with respect to the oxygens and the two terminal titanium atoms being five-coordinate. Raman, ir, and nmr data also support this structural assignment.

Although a large number of transition metal alkoxides are known[1] and have been used for a variety of purposes for decades, only in the rather recent past have attempts been made to study the structures of the polymeric species which are soluble in the common organic solvents. One of the few X-ray crystal studies of such compounds has been performed by Ibers,[2] who determined that titanium tetraethoxide in the solid state exists as a tetramer represented by $Ti{-}O_6$ octahedra sharing edges. A similar structure has been assigned to the solid methoxide[3] derivative.

A large number of benzene-soluble alkoxides have been studied in solution cryoscopically and ebulliometrically by Bradley and others. Bradley[4] has proposed a structural theory which relates the coordination number, stereochemistry, and the minimum degree of polymerization of polymeric alkoxides. Specifically it has been asserted that metal alkoxides adopt the smallest possible structural unit consistent with all of the metal atoms attaining a higher coordination number. Choice of structure is limited also by the condition that the coordination number of oxygen not exceed four.

For example, Bradley and Westlake[5] have predicted that a trimer should predominate in solutions of titanium tetraethoxide since such a structure will allow all titanium atoms in the molecule to be six-coordinate. The structure proposed can best be described as a linear molecule with three TiO_6 octahedra sharing faces. Yet, it is apparent that a tetramer exists in the solid state, not a trimer.

All structural assignments for titanium tetraethoxide in solution have been based heavily upon cryoscopic and ebulliometric measurements. Unfortunately, agreement upon molecular weight values from study to study has not been good. For instance, it has been reported that the molecular weight in benzene varies with time[6] and that after several hours the substance behaves as a monomer. Other workers have claimed that extensive depolymerization[7,8] occurs in dilute benzene solutions. More recently, Bradley claimed that the degree of aggregation is precisely three and is concentration-independent.[9] Early structural studies were not especially successful. Dipole moments[10–12] reported for titanium alkoxides ranged in value between 1.0 and 2.0 D. Interpretation of these data in terms of structure has been

---

(1) D. C. Bradley, "Progress in Inorganic Chemistry," Vol. 2, Interscience Publishers, New York, N. Y., 1960, p 353.

(2) J. A. Ibers, *Nature*, **197**, 686 (1963).

(3) R. W. Adams and G. Winter, *Aust. J. Chem.*, 20, 171 (1967).

(4) D. C. Bradley, *Nature*, **182**, 1211 (1958).

(5) D. C. Bradley and A. H. Westlake, *ibid.*, **191**, 273 (1961).

(6) A. N. Nesmeyanov, O. V. Nogina, and V. A. Dubovitskii, *Dokl. Akad. Nauk. SSSR*, **128**, 964 (1959).

(7) C. N. Caughlan, H. S. Smith, W. Katz, W. Hodgson, and R. W. Crowe, *J. Amer. Chem. Soc.*, 73, 5652 (1951).

(8) R. L. Martin and G. Winter, *Nature*, **197**, 687 (1963).

(9) D. C. Bradley and C. E. Holloway, *Inorg. Chem.*, 3, 1163 (1964).

(10) B. A. Arbusov and T. G. Shavsa, *Dokl. Akad. Nauk SSSR*, **68**, 859 (1949); *ibid.*, **79**, 559 (1951).

(11) R. W. Crowe and C. N. Caughlan, *J. Amer. Chem. Soc.*, 72, 1694 (1950).

(12) C. N. Caughlan, W. Katz, and W. Hodgson, *ibid.*, 73, 5654 (1951).

difficult because of large uncertainties in the magnitude of contributions to the dipole moment due to bond moments and atomic polarization. In the last reported effort to solve the problem, Weingarten and Van Waser[13] attempted a structural study of titanium tetraethoxide using pmr measurements. They observed rapid exchange of ethoxide groups, and, hence, were unable to make an unambiguous assignment of structure in solution.

In the study reported below, the structure of titanium tetraethoxide in cyclohexane and carbon tetrachloride solution has been assigned. The degree of polymerization has been determined by light-scattering turbidity measurements, and the molecular geometry has been ascertained unambiguously by the measurement of the intensity of depolarized Rayleigh-scattered light. The general method of structural analysis[14] used has been outlined previously.

Experimental Section

Light-Scattering Photometer. Intensities of horizontally and vertically polarized Rayleigh-scattered light were measured using a specially constructed photometer described elsewhere.[14] A Spectra-Physics Model 122 CW laser was used to provide a vertically polarized light source of wavelength 6328 Å. All depolarization measurements were made using a 30 × 30 mm cell purchased from the Phoenix Instrument Company. The cell was painted on the outside, except for the entrance and exit slits, with a flat black paint to minimize reflections. The calibration of the photometer was accomplished based on scattering from either pure cyclohexane or carbon tetrachloride as the occasion demanded. Solution refractive indices were measured by means of a Brice-Phoenix differential refractometer, Model BP-2000V.

Solution Clarification. Dust-free solutions were obtained by pressure ultrafiltration. A Gelman Model 4280 pressure filtration funnel equipped with a Millipore Corporation filter, Type VCW-PO4700 freed solutions from dust after three filtrations. However, as a general practice six or seven filtrations were performed on each solution and scattered-light intensities were measured after each filtration. Intensity minima were reproducible to 1–2%.

Filtration of titanium tetraethoxide solutions presented a difficult problem because the solute hydrolyzed upon contact with air even in solution. Naturally, colloidal hydrolysis products interfere with scattering results and must be removed completely. The only technique of the many tried that worked well involved filtration in an inert atmosphere box flushed with dry nitrogen and saturated with solvent vapor. By means of this method clarification of solutions was carried out with no interference from hydrolysis products.

Actually, it was found that the presence of a very few dust particles in the liquids studied did little harm. Due to the very small scattering volume subtended by the phototube the dust particles could be detected as "spikes" on the intensity *vs.* time plots. Contributions from reflections were very small.[14]

Reagents. Spectrograde solvents were purchased from Eastman Organics, Inc., and used with no further purification. Organotin compounds were purchased from Alfa Inorganics.

Titanium Tetraethoxide. Purified titanium tetrachloride (25 g) purchased from Eastern Scientific, Inc., was distilled directly into a dropping funnel attached to a three-neck reaction flask containing 150 g of dry ethanol. The titanium tetrachloride was added slowly to the ethanol over a period of 45 min with continuous stirring. Ammonia, which had been dried by first passing it through a 6-ft coiled column immersed in an ice bath and then through a trap held at −20° to remove all water, was added until a weight gain of 10 g was achieved. The mixture was then heated for 1 hr with an oil bath maintained at 70°. The mixture was allowed to reach room temperature and then filtered in the drybox. The filtrate was concentrated by means of a rotary evaporator and diluted with benzene to precipitate any residual halide. Pure titanium tetraethoxide was obtained by vacuum distillation. The fraction analyzed boiled at 128–129° with 1.5 mm pressure. *Anal.* Calcd: C, 42.13; H, 8.77. Found: C, 42.14; H, 8.79.

Raman and Infrared Spectra. Ir spectra in the 1200–250-cm^{-1} range were observed for pure liquid titanium tetraethoxide dispersed in Nujol and pressed between polyethylene disks. Raman spectra were determined for the pure liquid and a 50% cyclohexane solution. The Raman spectra were obtained on a Spex Ramalog spectrometer using the 5415-Å line of an argon laser as the exciting radiation. Strong absorptions of interest were noted in the ir at 590 and 715 cm^{-1}, while only one sharp peak at 615 cm^{-1} was observed in the Raman below 800 cm^{-1}. Ir spectra were run on a Perkin-Elmer 521.

Calculation of the Molecular Polarizability Anisotropy

Values of the polarizability anisotropy were calculated according to the method of Bothorel.[15] The pure solvents were used to calibrate the instrument to measure the Rayleigh ratio for both total scattering and anisotropic scattering. Turbidity values[16] reported by Carr and Zimm were used throughout.

Since the incident laser beam was vertically polarized the calculations had to be modified accordingly. Actually no change had to be made in the equations of Bothorel at all, but in the calibration of the instrument it had to be taken into account that $R_v = 2R_u/(1 + P_u)$. R_u and R_v are the Rayleigh ratios for the solvents interacting with unpolarized and vertically polarized light, respectively. P_u is the depolarization ratio for unpolarized light. Using the Carr and Zimm value for R_u and the Bothorel value for P_u one obtains for cyclohexane $R_v = 8.35 \times 10^{-6}$ at 5460 Å. Therefore, at 6328 Å R_v is 4.65×10^{-6}. For the horizontally polarized component of the light scattered from the laser beam

$$R_{iv} = (4.65 \times 10^{-6})\left(\frac{P_v}{1 + P_v}\right)$$

Since $P_v = 0.0304$, $R_{iv} = 13.5 \times 10^{-8}$ cm^{-1}.

For carbon tetrachloride using Carr and Zimm's value of 5.88×10^{-6} for R_u at 5461 Å and a value of 0.020 for P_v, $R_{iv} = 12.28 \times 10^{-8}$ cm^{-1}. To solve the Bothorel equation for the polarizability anisotropy the refractive index, n, of the solvent is required. Values were obtained from application of the Cauchy formula. Refractive indices at 6328 Å are, for cyclohexane, $n = 1.42489$; and for carbon tetrachloride, $n = 1.46060$.

Given the value of R_{iv} at 6328 Å for the solvent, the molecular optical anisotropy, γ^2, of a solute in solution with cyclohexane can be found easily from the experimentally measured intensity of the horizontally polarized light scattered from the solution. Given

$$R_{ivs} = \frac{i_s}{i_0} R_{iv}$$

where R_{ivs} = the Rayleigh ratio of horizontally polarized light scattered from the solution minus R_{iv}, R_{iv} = the Rayleigh ratio of the solvent assigned to horizontally polarized scattered light, i_s = the horizontally polarized scattered light intensity of the solution minus i_0 measured in relative units (mV signal), and i_0 = the horizontally polarized scattered light intensity of solvent (mV signal), then

$$\gamma^2 = \frac{135\lambda^4 R_{ivs}}{32\pi^4 p(n^2 + 2)^2}$$

---

(13) H. Weingarten and J. R. Van Waser, *J. Amer. Chem. Soc.*, **87**, 724 (1965).

(14) W. R. Russo and W. H. Nelson, *ibid.*, 92, 455 (1970).

(15) A. Ananué and P. Bothorel, *Bull. Soc. Chim. Fr.*, 573 (1964).

(16) C. I. Carr and B. H. Zimm, *J. Chem. Phys.*, **18**, 1616 (1950).

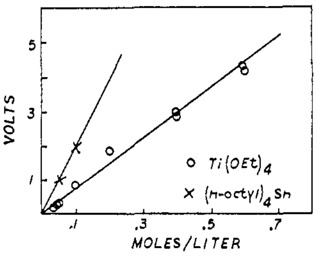

Figure 1. Increments in total scattering at 90° due to solute molecules.

Anisotropy values for titanium tetraethoxide are very large. (See Table I.)

Table I. Molecular Optical Anisotropy of Tetraethyl Titanate

Solvent	Concn, M	R_{iv}	R_{ivs}	γ^2, cm^6
Cyclohexane	0.03	0.400	0.140	1.11×10^{-46}
	0.05	0.400	0.230	1.11×10^{-46}
	0.10	0.400	0.450	1.09×10^{-46}
	0.20	0.400	0.920	1.14×10^{-46}
	0.40	0.400	1.68	1.09×10^{-46}
	0.60	0.400	2.49	1.11×10^{-46}
Carbon tetrachloride	0.10	0.860	1.15	1.15×10^{-46}
	0.20	0.860	2.21	1.13×10^{-46}
	0.60	0.860	6.05	1.11×10^{-46}

Molecular Weight Determinations

A molecular weight determination of titanium tetraethoxide was attempted using a Mechrolab Model 301A vapor pressure osmometer. In spite of the use of the inert atmosphere attachment, hydrolysis could not be prevented completely, and consequently the osmometer was placed in an inert atmosphere box which had previously been flushed with nitrogen and dried with P_2O_5. However, it was found impossible to operate the osmometer effectively under such conditions. Generally for hygroscopic materials we have found osmometry to be a very poor method of determining molecular weights.

The molecular weight of tetra-*n*-octyltin on the other hand was easily measured by the osmometer since the compound is relatively inert. Results at several concentrations in the vicinity of 0.1% solute by weight indicated a molecular weight of 570 as opposed to the calculated molecular weight of 571 for a monomer.

Because of the failure of the osmometry to determine the molecular weight of titanium tetraethoxide, turbidities of solutions were measured (Figure 1). From the turbidity difference between solvent and solutions, the molecular weight of molecules can be determined (Figure 2) in solution as follows

$$1/M_w = \frac{32\pi^3 n_0^2}{3\tau^4}\left(\frac{dn}{\partial c}\right)^2 \frac{c}{\tau^*}$$

The symbols have the standard meanings.[17] c is expressed in grams of solute per milliliter of solution.

The refractive index increments (Figure 3) were obtained using a Brice–Phoenix differential refractometer, Model 2161. Solutions for instrument calibration were prepared from dry KCl and distilled water.

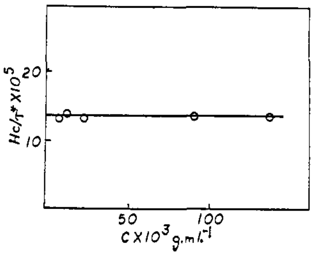

Figure 2. Hc/τ^* *vs.* concentration plot for titanium tetraethoxide in cyclohexane. Hc/τ^* equals $1/M$ at $c = 0$.

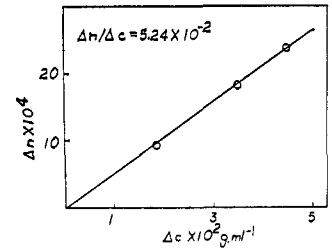

Figure 3. Plot of the increase in the refractive index, Δn, *vs.* the concentration, c, of titanium tetraethoxide in cyclohexane.

For the purposes of molecular weight determination the photometer was calibrated by measuring the scattering from solutions of a molecule of known molecular weight, tetra-*n*-octyltin. Since depolarization ratios were small for the molecules observed, turbidities were assumed to be proportional to the vertically polarized scattered light intensity at 90° to the incident beam. From the data summarized in Figures 1–3 it is apparent that the molecular weight of titanium tetraethoxide in cyclohexane solutions is 694 g/mol and that the molecule is a trimer over the range of concentrations studied.

To ensure that the turbidity measurements obtained were truly due to the solute, and not increased due to the presence of colloidal particles, turbidity measurements were made on a centrifuged and a noncentrifuged sample of tetra-*n*-octyltin. A sample centrifuged at 100,000*g* for 2 hr exhibited the same turbidity as one which had merely been subject to ultrafiltration. The fact that the plots of excess turbidity *vs.* concentration are linear and pass through the origin also indicates clear solutions.

Calculation of Bond Polarizabilities and Group Polarizabilities for Titanium Tetraethoxide

The Ti–O bond polarizabilities were calculated using a method described by Lippincott and Stutman.[18] Bond lengths used were obtained from the crystal X-ray work of Ibers. Calculated bond and group polarizability values appear in Table II. It is expected that differences between calculated and true values of the polarizability components will be in the vicinity of 10%. Bond polarizability values not appearing in Table II were taken from ref 18.

Calculation of Anisotropy Values for Candidate Titanium Tetraethoxide Structures

Several of the structures considered most likely candidates for describing titanium tetraethoxide in solution have been described by Van Waser.[13] These

---

(17) P. Debye, *J. Phys. Chem.*, **51**, 18 (1947).

(18) E. R. Lippincott and J. M. Stutman, *ibid.*, **68**, 2926 (1964).

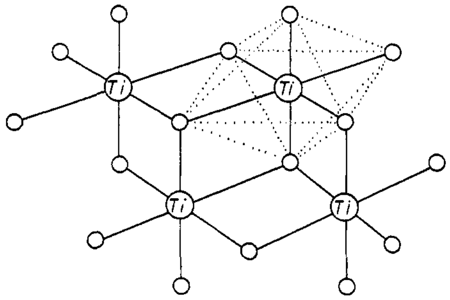

Figure 4. Crystal structure of $Ti(OEt)_4$.

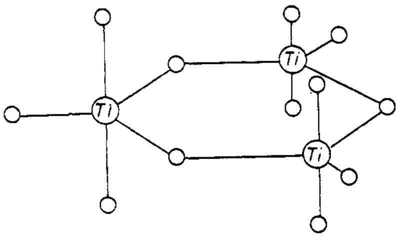

Figure 5. Structure I.

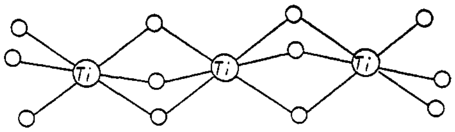

Figure 6. Structure II.

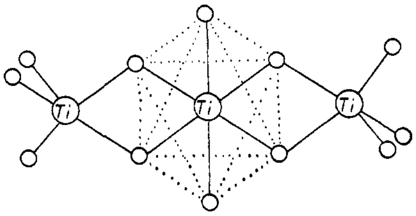

Figure 7. Structure III.

structures are shown along with Ibers' solid-state structure[2] in Figures 4–7. There is little doubt that the structure in solution is trimeric.

Table II. Calculated Group Polarizabilities

Group	$\alpha \times 10^{25}$ cm^3	$\alpha_\perp \times 10^{25}$ cm^3
Ti–O (bridged) bond	25.0	6.0
Ti–O (terminal)	17.3	6.0
Terminal ethoxide (free rotation about Ti–O bond)	47.2	50.6
Bridged ethoxide (free rotation about C–O bond)	56.5	46.0

Structure I. The principal axis (C_3) was chosen to be collinear with the z coordinate axis. It follows that there are five different Ti–O bond types, described in Table III. Then using the equations of Smith and Mortensen[19] one obtains, for the diagonalized polarizability tensor of the Ti–O skeleton, $\alpha_{xx} = 163.8 \times 10^{-25}$, $\alpha_{yy} = 164.0 \times 10^{-25}$, and $\alpha_{zz} = 157.8 \times 10^{-25}$ cm^3.

Table III. Ti–O Bond Types for Structure I

Bond type	Description	θ	ϕ
I	Four bridge bonds	90	60
II	Two bridge bonds	90	0
III	Two terminal bonds	90	60
IV	One terminal bond	90	0
V	Six terminal bonds	0	0

There are five different types of ethoxide groups described in Table IV. The net contribution of the ethoxide groups to the molecular polarizability can be diagonalized to give $\alpha_{xx} = 601.5 \times 10^{-25}$, $\alpha_{yy} = 606.8 \times 10^{-25}$, and $\alpha_{zz} = 573.0 \times 10^{-25}$ cm^3. Adding the diagonalized tensors one obtains, for the diagonalized molecular polarizability tensor, $\alpha_{xx} = 765 \times 10^{-2} = b_1$, $\alpha_{yy} = 771 \times 10^{-25} = b_2$, and $\alpha_{zz} = 731 \times 10^{-2}$ cm^3 $= b_3$. The anisotropy, $\gamma^2 = {}^1/_2[(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2] = 14.0 \times 10^{-48}$ cm^6.

Table IV. Ethoxide Groups of Structure I

Bond type	Description	θ	ϕ
I	One bridged group, rotation about C–O bond	90	0
II	Two bridged groups, rotation about C–O bond	90	60
III	One terminal group, rotation about Ti–O bond	90	0
IV	Two terminal groups, rotation about Ti–O bond	90	60
V	Six terminal bonds, rotation about Ti–O bond	0	0

Structure II. The z coordinate axis was chosen to include all three titanium atoms. The four different types of Ti–O bonds are shown in Table V. Using the method of Smith and Mortensen the net Ti–O contributions to the diagonalized polarizability tensor are $\alpha_{xx} = 218.0 \times 10^{-25}$, $\alpha_{yy} = 209.1 \times 10^{-25}$, and $\alpha_{zz} = 207.3 \times 10^{-25}$ cm^3. There will result four symmetrically different ethoxide groups described in Table VI. One then obtains for the ethoxide-group component of the diagonalized molecular polarizability tensor $\alpha_{xx} = 572.7 \times 10^{-25}$, $\alpha_{yy} = 604.8 \times 10^{-25}$, and $\alpha_{zz} = 573 \times 10^{-25}$ cm^3. For the molecular polarizability one then obtains the following components: $\alpha_{xx} = 790.7 \times 10^{-25} = b_1$, $\alpha_{yy} = 814.0 \times 10^{-25} = b_2$, and $\alpha_{zz} = 780.6 \times 10^{-25}$ cm^3 $= b_3$. The value of the anisotropy resulting is 9.0×10^{-48} cm^6.

Table V. Ti–O Bonds of Structure II

Bond type	Description	θ	ϕ
I	Two terminal bonds	54.5	0
II	Four terminal bonds	54.5	60
III	Four bridged bonds	54.5	0
IV	Eight bridged bonds	54.5	60

---

(19) R. S. Smith and E. Mortensen, *J. Chem. Phys.*, 32, 503 (1960).

Table VI. Structure II Ethoxide Groups

Bond type	Description	θ	ϕ
I	Two terminal groups, rotation about Ti–O bonds	54.5	0
II	Four terminal groups, rotation about Ti–O bonds	54.5	60
III	Two bridged groups, rotation about C–O bonds	90	0
IV	Four bridged groups, rotation about C–O bonds	90	60

Structure III. Structure III can be visualized as three polyhedra, a central octahedron, and two trigonal bipyramids, brought together in such a manner that they will share edges. By choosing again the molecular z axis to be collinear with the three titanium atoms, four different types of Ti–O bonds and four nonequivalent ethyl groups can be defined. The Ti–O bonds are described in Table VII. Components of the diagonalized tensor representing net Ti–O contributions are $\alpha_{xx} = 194.4 \times 10^{-25}$, $\alpha_{yy} = 141.4 \times 10^{-25}$, and $\alpha_{zz} = 194.4 \times 10^{-25}$ cm^3. There must be four symmetrically different ethoxide groups, described in Table VIII.

Table VII. Structure III Ti–O Bonds

Bond type	Description	θ	ϕ
I	Four terminal bonds	54.5	60
II	Two terminal bonds	54.5	0
III	Two bridged bonds	90	90
IV	Eight bridged bonds	45	0

Table VIII. Structure III Ethoxide Groups

Bond type	Description	θ	ϕ
I	Four terminal groups, rotation about Ti–O bond	54.5	60
II	Two terminal groups, rotation about Ti–O bond	54.5	0
III	Two bridged groups, rotation about C–O bonds	90	90
IV	Four bridged bonds, rotation about C–O bonds	90	0

The net contributions to the diagonalized polarizability matrix due to the ethoxide groups are $\alpha_{xx} = 643.0 \times 10^{-25}$, $\alpha_{yy} = 574.0 \times 10^{-25}$, and $\alpha_{zz} = 580.4 \times 10^{-25}$ cm^3. Combining the two contributions, the elements of the diagonal molecular polarizability matrix are $\alpha_{xx} = 837.4 \times 10^{-25} = b_1$, $\alpha_{yy} = 715.4 \times 10^{-25} = b_2$, and $\alpha_{zz} = 775.0 \times 10^{-25}$ cm$^3 = b_3$. The resulting calculated value of the anisotropy is 111.6×10^{-48} cm^6, a very large value.

Discussion

The Molecular Weight of Titanium Tetraethoxide. Before any candidate structures could be constructed for titanium tetraethoxide in solution a molecular weight determination was necessary. The molecular weight has been subject to some dispute. Reported values range from that of a monomer to a tetramer. Yet, most recent work seems to point to the existence of a trimer[9] in solution over a wide concentration range. This work shows that in cyclohexane titanium tetraethoxide is a trimer and that the degree of polymerization is concentration-independent over the concentration range studied.

Assignment of Structure to Titanium Tetraethoxide. Light-scattering data indicate rather definitely that the structure in solution is the one designated structure III. Neither of the other two candidate structures possesses a value of the anisotropy which is even close to the observed one.

A comparison of the Raman and ir absorption bands for the titanium tetraethoxide solutions shows that below 800 cm^{-1} there are no bands that coincide. This very likely indicates that the molecule in solution is centrosymmetric as is structure III but not structure I, the cyclic structure. A symmetry analysis of the normal vibrational modes of the Ti–O skeleton of structure I, which belongs to the point group D_{3h}, gives us the following reducible representation: $\Gamma = 8E' + 5A' + 3A' + A''_1 + 4A'_2$. Since the modes associated with the 8E′ are both ir and Raman active, it may be expected to give Raman and ir spectra quite different from those obtained even if one considers the possibility that not all the active vibrations would be observed.

Nmr work published earlier by Van Waser, *et al.*,[13] also is consistent with the assumption that structure III exists in solution. To be sure that work really eliminates only structure II of the candidate structures.

Past attempts to calculate bond polarizabilities using quantum mechanical principles have been less than completely successful. Yet, the Δ-function model does appear to be reasonably reliable since it has been used[15] to calculate molecular polarizabilities which compare favorably with experimental values for a wide variety of compounds. Undoubtedly this type of calculation may suffer uncertainties of 10–20%. But, it should be noted that for many interesting systems such certainty may be all that is needed.

It has been shown that the polarizability anisotropy is quite sensitive to molecular geometry, but not nearly as sensitive to the exact magnitude of the bond polarizability. This is basically due to the fact that most bonds are much more polarizable in a direction along the bond (longitudinal polarizability) than they are in a direction perpendicular to the bond (transverse polarizability).

Since bond polarizabilities are strongly a function of bond lengths, choices of bond lengths must be explained. Over the past several years it has been demonstrated[20] that metal–oxygen bond lengths in isopolyacids are strongly a function of environment, but that they depend in a predictable way upon the number of metal atoms to which the oxygen is bound. Thus, it is reasonable to assume a characteristic value for a Ti–O bond length obtained from X-ray work[2] depending upon whether the ethoxide concerned is a terminal group or a bridging group.

The value of the coordination number in the various structures probably deserves some comment. Of the various structures only structure II achieves a maximum coordination number of six for titanium. It might at first appear that such a structure should be the

---

(20) M. T. Pope and B. W. Dale, *Quart. Rev.* (London), 527 (1968).

most stable. However, a structure described in terms of octahedra sharing faces would force the titanium atoms so close together, 2.3 Å, if normal Ti–O bond distances are maintained, that there is no doubt that such a structure would be one of very high energy. Bringing titanium atoms close enough together to actually touch would mean increasing the repulsion energies of such like-charged atoms greatly. It is probably due to such interactions that isopolyacids of groups IV, V, and VI adopt structures best represented by octahedra sharing edges rather than faces. It is probable also that the degree of polymerization of this alkoxide in solution is three for steric reasons. That polymerization of titanium alkoxides is affected by the bulk of the alkoxide group is known from previous work.[1]

The findings of the present study tend to be entirely consistent with the general structural theory of Bradley, which predicts that metal alkoxides will form stable polymeric species having the minimum degree of polymerization consistent with the achievement of a maximum characteristic coordination number for the metal "ion." To be sure the maximum coordination number of titanium in such compounds appears to be six, and it is reasonable to assert that the tetramer appears in the solid state because it is the lowest molecular weight molecule, with reasonable Ti–O and Ti–Ti atom distances, which can be constructed with titanium of coordination number six. Upon melting, however, and in solution it is suggested that the additional degrees of freedom allowed due the ethoxide group rotations result in the stabilization of the trimeric molecule with respect to the tetramer.

The likelihood of substantial error in the Ti–O longitudinal bond polarizability value used is readily acknowledged, since bond lengths used were taken from the solid state study of Ibers, which involved only six-coordinate titanium. If the calculated molecular anisotropies of the three structures were not substantially different from one another the correct structural assignment might have been difficult. However, the calculated anisotropy of structure III is clearly so much larger than that of the other two and so close to the measured value that huge errors in the Ti–O bond polarizability would have to be invoked to result in a mistaken assignment. It appears rather certain that the structure in solution is structure III. It should be noted that the measurement of the optical anisotropy, γ^2, alone allowed the unambiguous selection of the proper structure. It is anticipated that many other structures of practical or theoretical interest presently inaccessible to determination in solution will be studied successfully using the method discussed.

Acknowledgment. Thanks are due to Research Inc., for generous support during the early stages of this study. Much appreciated help also has been received from the National Science Foundation through GP-5880. Valuable advice concerning construction of the photometer was generously given by Dr. J. L. Lundberg.

A Phase Investigation of the Ytterbium–Carbon System

John M. Haschke and Harry A. Eick[1]

Contribution from the Department of Chemistry,
Michigan State University, East Lansing, Michigan 48823.

Received September 15, 1969

Abstract: The ytterbium–carbon system, YbC_x, has been investigated over the composition range $0.33 \leq x \leq 2.00$; samples were prepared by direct reaction of the elements in sealed tantalum bombs. Four phases have been identified by X-ray diffraction and elemental analysis: tetragonal $YbC_{2.00}$ ($a = 3.639 \pm 0.003$, $c = 6.110 \pm 0.008$ Å), monoclinic $YbC_{1.25+y}$ with $0 \leq y \leq 0.16$ ($a = 7.070 \pm 0.005$, $b = 7.850 \pm 0.004$, $c = 5.623 \pm 0.005$ Å, $\beta = 90.99 \pm 0.09°$, for samples quenched from 1450°K), $YbC_{0.95}$, and dimorphic $YbC_{0.50\pm z}$ (fcc, $a = 5.001 \pm 0.003$ Å and rhombohedral, $a = 6.167$ Å, $\alpha = 33.33°$). A linear variation of both the carbon-rich $YbC_{1.25+y}$ phase boundary and the monoclinic b parameter with temperature has been observed. A partial phase diagram for the Yb–C system is proposed, and the variation of composition and lattice parameter of the $YbC_{1.25+y}$ phase is discussed.

From a structural investigation of the lanthanide carbides Spedding, *et al.*,[2] reported for ytterbium the dicarbide, a trimetal monocarbide, and "an intermediate carbide" of undetermined composition. More recent studies on this system have been concerned with the carbon-rich phases. Krikorian, *et al.*,[3] investigated the dicarbide–carbon eutectic and searched for a tetragonal–cubic dicarbide transition. Haschke and Eick[4] presented evidence for a two-phase region between $YbC_{1.5}$ and YbC_2, and consequently for the existence of a sesquicarbide. The present investigation was initiated to examine the metal-rich portion of the ytterbium–carbon system and, in particular, to characterize the phase diagram near the sesquicarbide composition.

---

(1) To whom inquiries should be addressed.

(2) F. H. Spedding, K. Gschneidner, Jr., and A. H. Daane, *J. Amer. Chem. Soc.*, 80, 4499 (1958).

(3) N. H. Krikorian, T. C. Wallace, and M. G. Bowman, Proceedings, Colloque International Sur les Derives Semimetallique du Centre National de la Recherche Scientifique et Universite du Paris, Orsay, 1965.

(4) J. M. Haschke and H. A. Eick, *J. Phys. Chem.*, 72, 1697 (1968).