

C-O and Ti-O VIBRATION FREQUENCIES IN ALKYL TITANATES*

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In a previous communication¹ it was shown that titanium(IV) methoxide exists in two modifications. The microcrystalline form (A) is insoluble in most organic solvents, while the other form (B) is obtained in large crystals from boiling toluene. It was also shown that in the 600–200 cm^{-1} region, where one may expect to observe the Ti-O vibrations, the absorption spectra differed markedly, but no attempt was made to assign the observed bands.

The crystal structure of form (B) has now been reported by Wright² who showed that it is very similar to titanium(IV) ethoxide determined by Ibers.³ A salient feature of these structures is the presence in both of three different classes of oxygen-titanium bond. The oxygen atoms of apex and equatorial terminal groups each interact with one titanium atom (TiOR), four of the six oxygen atoms in bridging positions are bonded to two titanium atoms (Ti_2OR), while the other two are common to three titanium atoms (Ti_3OR). We have now examined in detail the infrared spectra in Nujol of the two forms in the 1200–1000 cm^{-1} region where the C-O stretching frequencies occur,^{4–6} in order to examine the dependence of the frequency on the type of oxygen interaction.

The spectrum of form (A) (see Fig. 1) is in substantial agreement with that reported by Kriegsman and Licht⁴ whose material was prepared in the same manner as our form (A). The two bands at 1085 and 1040 cm^{-1} are assigned to two C-O stretching frequencies, the former arising from TiOR (terminal) groups and the latter from Ti_2OR (bridging) groups. In form (B) these two bands are very slightly displaced and an additional strong band at 995 cm^{-1} is observed. We believe that this new band should be assigned to the C-O frequency of the Ti_3OR groups.

Titanium(IV) ethoxide exists as a crystalline solid³ and a supercooled liquid at room temperature. Grinding the former in Nujol produces a cloudy suspension which becomes clear on heating. The liquid dissolves to clear solution in Nujol. In Figure 2, the spectra of the liquid form in Nujol (a), the solid in Nujol after heating (b), the solid in a KBr disk (c), and the solid as a suspension in Nujol (d) are compared. The spectra of the solid (in KBr or Nujol) show a band at 1050 cm^{-1} (1045 cm^{-1}), which is barely present in the Nujol solution of the liquid form and practically

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¹ Adams, R. W., and Winter, G., *Aust. J. Chem.*, 1967, **20**, 171.

² Wright, D. A., and Williams, D. A., *Acta crystallogr.*, 1966, **21**, A155.

³ Ibers, J. A., *Nature*, 1963, **197**, 886.

⁴ Kriegsman, H., and Licht, K., *Z. Electrochem.*, 1958, **62**, 1163.

⁵ Barraclough, C. G., Bradley, D. C., Lewis, J., and Thomas, I. M., *J. chem. Soc.*, 1961, 2601.

⁶ Bradley, D. C., and Westlake, A. H., *Proc. Symposium on Co-ordination Chemistry*, Tihany, Hungary, 1964.

disappears on heating the Nujol suspension of the solid form. This band had previously been assigned^{5,6} to the C-O stretching mode of the bridging ethoxy group, and we now suggest that it is specifically that of the Ti_3OEt group. The displacement by about 50 cm^{-1} towards higher energy as compared to the corresponding band in the methoxide, is qualitatively in accord with the longer alkyl group. The variation in intensity of the bands at 1100 cm^{-1} in the liquid and solid ethoxide is evidence for the formation of additional terminal ethoxy groups⁶ resulting from the breaking of ethoxy bridges.

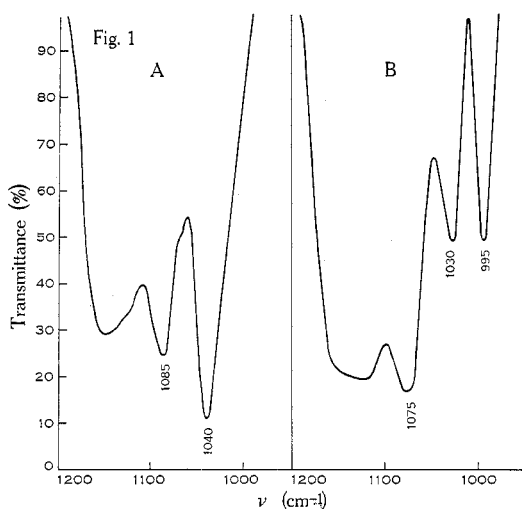
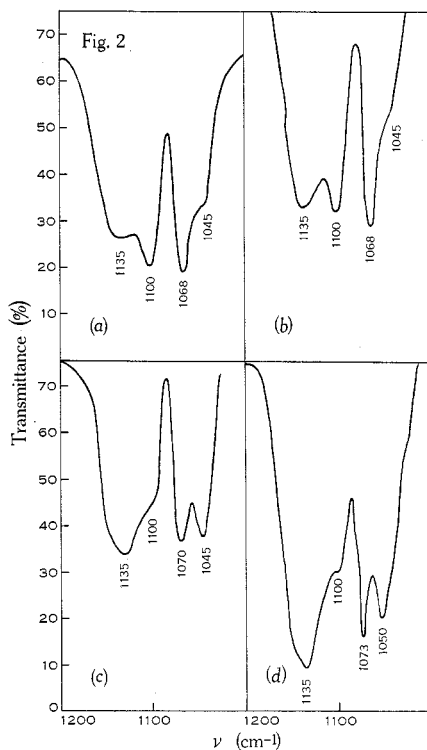


Fig. 1.—I.r. absorption of titanium(IV) methoxide; forms A and B (see text).

Fig. 2.—I.r. absorption of titanium(IV) ethoxide.

- (a) Liquid form in Nujol;
- (b) solid form in Nujol after heating;
- (c) solid form in KBr disk;
- (d) solid form as suspension in Nujol.



Preliminary results of an X-ray structure determination of the solid hydrolysis products of titanium(IV) ethoxide have recently been reported by Watenpaugh and Caughlan.⁷ It is a heptamer with structural features similar to those of the parent compound, but with Ti_3O and Ti_4O replacing the Ti_3OR groups. In accordance with our assignment of the 1045 cm^{-1} band to the C-O stretching mode of the Ti_3O groups, we find that this band disappears on partial hydrolysis of titanium(IV) ethoxide, and two new bands at 780 and 725 cm^{-1} appear. We suggest that these latter two absorption bands are the Ti-O stretching modes of the Ti_3O and Ti_4O groups. The

⁷ Watenpaugh, K., and Caughlan, C. N., *Chem. Commun.*, 1967, 76.

corresponding mode in the Ti_2O group has previously been assigned to various bands around 800 cm^{-1} .^{8,9}

Finally, $\text{TiCl}_2(\text{OEt})_2 \cdot \text{EtOH}$ is known to be dimeric¹⁰ so that the alkoxy groups would be involved in terminal TiOR and Ti_2OR bridges. The infrared spectrum of this compound shows absorption bands at 1105 and 1065 cm^{-1} but there is no absorption at 1045 cm^{-1} . There is a band at 1020 cm^{-1} and this is attributed to the C—O vibration of the coordinated alcohol.¹¹

⁸ Zeitler, V. A., and Brown, C. A., *J. phys. Chem.*, 1957, **61**, 1174.

⁹ Bradley, D. C., and Westlake, A. H., *Nature*, 1961, **191**, 273.

¹⁰ Brown, R. N., and Winter, G., *J. chem. Soc.*, 1963, 734.

¹¹ Kakos, G. A., Kruger, A. G., and Winter, G., unpublished data.