

axis in Fig. 1, this ratio is 1.4, thus the groups contain three nuclei. The full line represents the growth of three hemispherical nuclei at the apices of an equilateral triangle with proper allowance for single and multiple overlap. Calculations for three nuclei in a straight line do not accord with this.

A non-random arrangement of nuclei is thus adequate to explain these kinetic features. It is not necessary to introduce non-isothermal conditions or rapid growth of small nuclei.

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Brown (β) Titanium Trichloride

RECENT papers by Clark¹ and Dijkgraaf² have shown that α -TiCl₃ may be distinguished from β -TiCl₃ by differences in the reflectance spectra of the two solids. In particular, the band at 19,000 cm⁻¹ in the violet (α) form is replaced by a band at 24,000 cm⁻¹ in the brown (β) form.

I have now found that the violet and brown aqueous acid solutions of the respective α and β forms can be distinguished from one another by absorption maxima at frequencies similar to those of the two solids (Table 1).

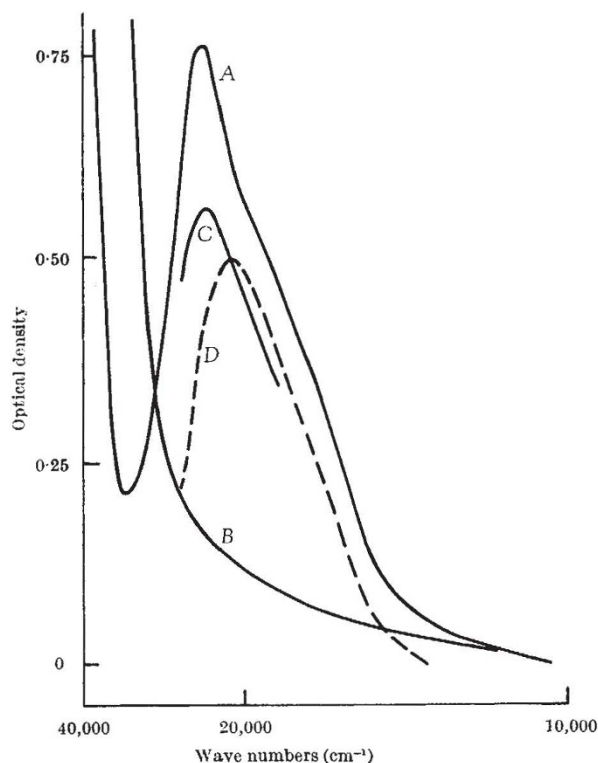


Fig. 1. Oxidation and reduction of a solution of brown (β) TiCl₃ (9.6 mg/ml. in 1.3 N sulphuric acid)

A, fresh solution; B, solution A after passage of oxygen for 30 min; C, solution B after cathodic reduction; D, solution B after prolonged oxidation and subsequent cathodic reduction

Table 1. ABSORPTION SPECTRA OF TiCl₃ IN 1.3 N SULPHURIC ACID

Form	Concentration (mg/ml.)	Wave numbers of absorption maxima (cm ⁻¹ × 10 ⁻²)	Colour
α	12.0	193 (Σ 3)	Violet
β	9.6	233 (Σ 14)	Brown

* Indicates an inflexion on a larger curve; Σ indicates extinction coefficient per 154 g of solute.

Distinctive spectra can also be obtained from solutions of the two forms in ethanol and acetonitrile.

These observations suggest that β -TiCl₃ preserves some of its distinctive structure in solution even when the medium is strongly solvating. A remarkable example of the stability of this role structure is provided by a solution of β -TiCl₃ which has been subjected to an oxidation-reduction sequence (Fig. 1). It could well be assumed that such a succession of chemical reactions would convert any trivalent titanium into its most stable form; indeed, after anodic oxidation for several days the violet coloration of α -TiCl₃ is produced on cathodic reduction. If, however, the duration of the oxidized stage is limited to 1 h, it is surprising to find that the brown coloration is restored by cathodic reduction.

Further work on the structure of β -TiCl₃ is in progress.

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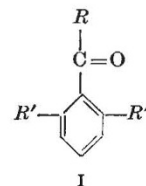
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Tetracyanoethylene Complexes as Indicators of the Carbonyl Inductive ($-I$) Effect in Sterically Hindered Aromatic Ketones

It is well established that the conjugation of the carbonyl group with the aromatic π -electron system in alkyl phenyl ketones (I, $R' = R'' = H$) is not hindered by the substitution of one methyl group in the *ortho*-position (I, $R' = CH_3$, $R'' = H$).



However, two such *ortho*-substituted methyl groups (I, $R' = R'' = CH_3$) force the oxygen of the carbonyl group out of the plane of the aromatic ring and so suppress carbonyl-ring conjugation. This is shown by the large diminution in the intensity of the ultra-violet absorption in the region 210–300 m μ , in the 2,6-dimethyl compounds, relative to the 2-methyl- and unsubstituted compounds¹.

In principle, it should be possible to separate the inductive effect ($-I$) of the carbonyl group (independent of conjugation) from its mesomeric effect ($-M$) (dependent on conjugation) in several ways and so to observe the inductive effect independently in compounds of this type. Dipole moment investigations have achieved this². Thus the moments of 2-methylacetophenone and 2,6-dimethylacetophenone are respectively 3.22 D ($-I$ and $-M$ operating) and 2.81 D ($-I$ only operating).

Hammett σ -value investigations have also been directed to this general problem. Thus the value ($\sigma_p - \sigma_m$) generally gives a semi-quantitative measure of the separate effects, but this is only approximate³.

It was shown in 1937 by dipole moment investigations^{4c} that conjugation between the nitro-group and the aromatic ring in nitrodurene (3-nitro-1,2,4,5-tetramethylbenzene) is suppressed because the oxygen atoms of the nitro-group are forced out of the plane of the ring by the steric hind-