able.[33] He illustrated this by the smooth relation he found between Hammett's constants and ν(C=O) for substituted benzoic acids. Davison[34] found a similar relationship to exist for substituted dibenzoyl peroxides and peresters.

The results we have obtained for substituted benzophenones and acetophenones add to the experimental data and enlarge the basis for the parallelism Davison found between his results and Flett's. Figure 5 summarizes the results obtained by Flett, Davison and ourselves. We have chosen to use a straight line as the functional relation best suited to express the results rather than to use curves such as Flett and Davison used. The ordinate and abscissa scales are chosen so that the uncertainty of the data is expressed by the size of the circular dots on the graph. The slope of the line for each set of data is almost the same, being about 15 cm.$^{-1}$ per sigma unit.

Jaffe has recently shown that σ is a monotonic function of electron density for *meta* and *para* substituted benzene ring compounds.[35] This adds importance to the infrared approach to measuring Hammett's constants.

Acknowledgment.—We should like to express our appreciation to Drs. Farber, Fieser, French, Hart, Iball, Julian, Lagemann, Mariella, Pearson and Soloway, who so generously supplied us with the compounds included in this study. We should like to thank Miss Jean-Marie Lebas, Miss Mary Edwards and Mr. David A. Danley for their help in obtaining some of the spectra. This investigation was supported by a Frederick Gardner Cottrell research grant from the Research Corporation.

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[33] M. St. C. Flett, *Trans. Faraday Soc.*, **44**, 767 (1948).

[34] W. H. T. Davison, *J. Chem. Soc.*, 2456 (1951).

[35] H. H. Jaffe, *J. Chem. Phys.*, **20**, 279 (1952).

NASHVILLE, TENNESSEE

[CONTRIBUTION FROM THE SOUTHERN REGIONAL RESEARCH LABORATORY][1]

The Composition of Some Tetra-*t*-butyl Titanate–Glycol Reaction Products[2]

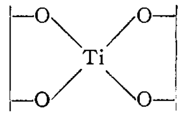
BY RICHARD E. REEVES AND LAURENCE W. MAZZENO, JR.

RECEIVED SEPTEMBER 28, 1953

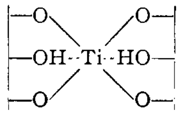
Accurate cryoscopic measurements can be made with tetra-*t*-butyl titanate (T*t*BT) in highly purified *t*-butyl alcohol. Such measurements on solutions of T*t*BT with ethylene glycol, octylene glycol or butanediol indicate the formation of molecular aggregates considerably larger than would occur if T*t*BT combined with one or two moles of glycol. Evidence is presented which strongly indicates the formation of a compound having the titanate:glycol ratio of 2:3; the species formed may actually contain 4 moles of titanate and 6 of glycol. The formation of other compounds having the compositions 2:2, 2:4 and 3:6 is also suggested. Thus it appears that T*t*BT does not form simple chelates with one or two bidentate glycol residues attached to a central titanium atom. On the other hand T*t*BT appears to react with ethyl acetoacetate to form 1:1 and 1:2 compounds. The present observations are discussed in relation to certain structural proposals which have appeared in the literature.

Tetraalkyl titanates are known to react with hydroxyl-containing polymeric substances such as cellulose acetate, cellulose nitrate and polyvinyl alcohol to produce insolubilization of the polymer. This effect has been attributed to titanium cross-linkages between the unsubstituted hydroxyl groups of two polymeric chains. Two structures which have been proposed to represent this interaction are shown below. Structure I, attributed by Schmidt[3] to Bayer and Nelles, involves a tetra-coördinated titanium atom bound to two hydroxyl groups on each of two polymer chains; while II, proposed by Schmidt, involves hexa-coördinated titanium bound to three hydroxyl groups on each polymer chain.

I



II



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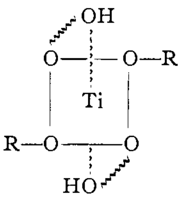
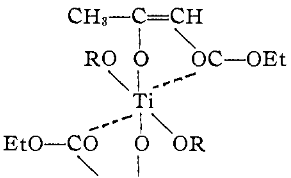


IV



Haslam[4] has studied the heats of reaction when tetraalkyl titanates react with certain bidentate groups and has attributed the large heats of reaction to the formation of stable chelate rings. It is known that the titanates undergo alcoholysis reactions with simple alcohols very readily, therefore it was reasonable to suppose that reaction with dihydroxy substances might produce chelate rings with a central titanium atom bound to one, two, or even three bidentate groups. Haslam found that most of the heat was evolved upon addition of two moles of bidentate ligand, hence he advanced structure III to represent his compounds. In this structure the wavy lines represent the hydrocarbon skeleton of a bidentate ligand such as octylene glycol. Schmidt[3] used a similar chelate structure, IV, to represent the product formed by the reaction of tetra-*n*-butyl titanate with two moles of ethyl acetoacetate.

It occurred to us that further information on the titanate–glycol and titanate–polymer structures might be obtained, advantageously, by means of

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[1] One of the laboratories of the Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

[2] Presented at the Regional Conclave of the American Chemical Society, New Orleans, La., December, 1953.

[3] F. Schmidt, *Angew. Chem.*, **64**, 536 (1952).

[4] John H. Haslam, a manuscript entitled "Correlation of Properties of Titanium Esters with Structure" presented before the Division of Organic Chemistry at the 122nd Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1952.

cryoscopic measurements in *t*-butyl alcohol solution employing the particular titanate, tetra-*t*-butyl titanate (T*t*BT). Getman[5] has recommended the use of *t*-butyl alcohol (trimethylcarbinol) as a cryoscopic solvent, citing as advantages its relatively high cryoscopic constant, and the fact that its melting point occurs, approximately, at room temperature. An additional advantage for the present work lies in the fact that *t*-butyl alcohol which may occur as a product of the reaction between T*t*BT and a ligand would not appreciably affect the freezing point depression of the solvent. The observed depression should directly reflect the size of any titanate–ligand combination which might occur in the solution. This report deals with the reaction between T*t*BT and three simple glycols; additionally, a small amount of work was done with ethyl acetoacetate in order to test the validity of structure IV.

Experimental[6]

t-Butyl alcohol was purified by fractional crystallization and by fractional distillation through a thirty-five plate Oldershaw column. It had a freezing point of 25.6°; less pure material was unsatisfactory for use in freezing point experiments with T*t*BT. The ethylene glycol contained 1.2 g. of water per liter (Karl Fischer procedure). D-(−)-Butanediol-2,3 was fractionally distilled and stored in a desiccator. The pure liquid had an optical rotation of −12.6° (1 dm.) indicative of relatively pure D-isomer; the rotation given in the literature for the pure substance is −13.19.[7] In *t*-butyl alcohol solution its specific rotation was −9.8° (*c* 2.47). The octylene glycol, a commercial product, was used without further purification. This material is stated by the manufacturer to be 2-ethylhexanediol-1,3, and since this structure contains two asymmetric carbon atoms it may be a mixture of two diastereomeric compounds. Ethyl acetoacetate was purified by vacuum fractional distillation, as was the T*t*BT. The latter was stored in a brown bottle kept in a desiccator.

Freezing points were measured with a Beckmann thermometer or with a calibrated thermometer graduated in $^1/_{10}$th degrees which could be read to 0.02° by the use of a lens. Provision was made for a blanketing atmosphere of dry air over the solutions while mixing and while freezing point measurements were in progress. To prevent excessive supercooling it was sometimes desirable to leave a tiny crystal of *t*-butyl alcohol adhering to the wall of the vessel above the level of the liquid. When the temperature of the liquid had dropped below its freezing point the crystal was introduced by means of the stirrer.

Stock solutions of the various ligands in *t*-butyl alcohol were prepared and the solutions were stored in a dry atmosphere. The compositions of these solutions, expressed in moles of solute per 1000 g. of *t*-butyl alcohol, were as follows: ethylene glycol, 0.572; octylene glycol, 0.600; butanediol, 0.622; ethyl acetoacetate, 0.641. For each ligand a solution of T*t*BT in *t*-butyl alcohol of exactly equal molality was prepared, and a series of solutions was made in side-arm test-tubes which were stoppered and placed in a desiccator at room temperature until the freezing point determinations were to be made. A slow current of dry air was then introduced through the side arm, the thermometer and stirring assembly was inserted, and the tube was placed in an air-bath surrounded by water at a temperature 3 to 5° below the freezing point.

The Effect of Time after Mixing on the Freezing Points.—Ethylene glycol–T*t*BT solutions gave the same results immediately after mixing and after standing for about two hours at room temperature. Butanediol–T*t*BT solutions kept the same freezing points for 24 hours, except at those mole fractions where precipitation occurred. The possible effect of time on the octylene glycol–T*t*BT solutions was not investigated; the recorded measurements were made about two hours after mixing.

The freezing points of the ethyl acetoacetate–T*t*BT solutions increased markedly during the first few hours after mixing, and then became relatively constant. The recorded measurements were made after 18 hours.

Optical rotation measurements were made at 25 ± 2° with a Gaertner polarimeter using the sodium D-line. The solutions were placed in stoppered cells and, except while under observation, were not exposed to light.

The Insoluble T*t*BT–Butanediol Compound.—To 7.8 g. of D-butanediol dissolved in 25 ml. of *t*-butyl alcohol was added 14.7 g. of T*t*BT (0.5 mole). The solution became warm and clusters of crystals formed within two minutes. After standing overnight at room temperature the precipitate was filtered, rinsed with several small portions of *t*-butyl alcohol, and dried in vacuum over P_2O_5 at room temperature. There was no further loss of weight in a sample dried in high vacuum at 78°. The yield amounted to 9.5 g. The product was soluble in benzene and chloroform, but not readily soluble in acetone or petroleum ether. It could be recrystallized from *t*-butyl alcohol with a considerable loss of material. It was not volatile in high vacuum up to 150°; it decomposed without melting when strongly heated. The initial specific rotation of this substance in dry chloroform was −50° changing slowly during 30 hours to a stable value of −54° (*c* 2.7). In dry benzene the initial value was −48° (*c* 2.4) with slight levo mutarotation on standing.

Anal. Calcd. for $C_{32}H_{68}O_{14}Ti_3$ (820.6): C, 46.84; H, 8.35; Ti, 17.51. Found: C, 46.57; H, 8.15; Ti, 17.5 (from TiO_2 ash after digestion with nitric acid); mol. wt. (cryoscopic) in benzene, 690 ± 10 (20 minutes after solution), 660 ± 10 (after 2 hours).

Discussion of Results

The freezing point depression curves for T*t*BT, ethylene glycol, butanediol and ethyl acetoacetate in *t*-butyl alcohol are shown in Fig. 1. The T*t*BT gave the normal freezing point depression constant (K_f = 8.4) over a fairly wide range of concentrations. This is evidence that it has no pronounced tendency toward association, a result which is in agreement with the work of Cullinane and co-workers.[8] The glycols appeared to have K_f values slightly higher, about 8.8, which may be indicative of a small amount of association with the solvent.[5] Ethyl acetoacetate showed upward curvature of its freezing point depression *vs.* concentration curve, behavior which is indicative of self-association, except at extreme dilution.

Figure 2 shows the results of cryoscopic measurements on mixtures of T*t*BT with each of the three glycols (curve A), and with ethyl acetoacetate (curve B). The abscissa represents mole fraction ligand, *i.e.*, the fraction of the total solute contributed by the ligand. The ordinate represents freezing point depression calculated to a one molal basis. The actual measurements were made at approximately 0.6 molality, but all were recalculated to the basis of one mole total solute per 1000 g. of *t*-butyl alcohol in order to facilitate the presentation of the results in a single figure. These curves amount to continuous variation experiments showing the change in freezing point as the Y

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(5) F. H. Getman, THIS JOURNAL, **62**, 2179 (1940).

(6) The *t*-butyl alcohol, ethylene glycol and ethyl acetoacetate were Eastman Kodak Co. products. D-(−)-Butanediol-2,3 was obtained from the Northern Regional Laboratory through the courtesy of Dr. R. W. Jackson. Octylene glycol was obtained from the Carbide and Carbon Chemicals Co. through the courtesy of Mr. John A. Field. Tetra-*t*-butyl titanate was furnished by E. I. du Pont de Nemours and Co. through the courtesy of Dr. John H. Haslam of the Experimental Station. The mention of a trade product does not imply its endorsement by the U. S. Department of Agriculture over similar products not named.

(7) J. W. Knowlton, N. C. Schieltz and D. Macmillin, THIS JOURNAL, **68**, 208 (1946).

(8) N. M. Cullinane, S. J. Chard, G. F. Price, B. B. Millward and G. Langlois, *J. Appl. Chem.*, **1**, 400 (1951).

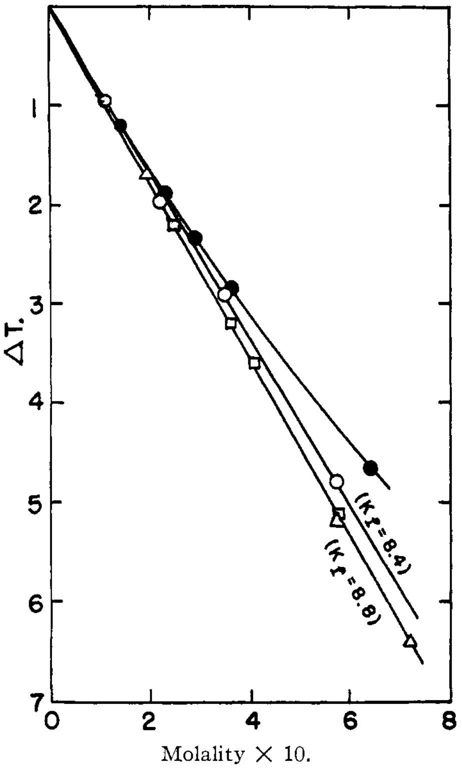


Fig. 1.—*t*-Butyl alcohol freezing point depression curves for solutions of T*t*BT (open circles), butanediol (squares), ethylene glycol (triangles) and ethyl acetoacetate (solid circles).

coördinate. Curve A clearly shows a peak at 0.6 mole fraction ligand corresponding to the formation of a complex containing T*t*BT and glycol in the ratio 2:3. The peak in curve B (ethyl acetoacetate ligand) occurs at 0.67 mole fraction ligand corresponding to the 1:2 ratio, but there is also a rather definite break in the curve at 0.5 mole fraction corresponding to the 1:1 ratio.

Figure 2 contains no data for butanediol between mole fractions 0.6 and 0.83. In this region these solutions became cloudy and freezing points were erratic; upon standing, crystalline material separated from the solutions. Such measurements as were made very soon after mixing gave points lying well above curve A, and having a maximum at 0.67 mole fraction ligand (T*t*BT : butanediol ratio 1:2).

Of the four ligands only the butanediol was optically active and afforded the opportunity for polarimetric study paralleling the cryoscopic investigations. It was possible to make observations immediately after mixing at any desired mole fraction of ligand, but the solutions above mole fraction 0.6 soon developed precipitates which obscured further observation. The polarimetric results are shown in Fig. 3. The abscissa, again, is mole fraction ligand, while the ordinate represents difference in rotation from that expected if no complexing had occurred. The results strongly indicate that formation of a complex at mole fraction 0.6 (T*t*BT:butanediol ratio 2:3) occurs immediately upon mixing.

Analyses of the insoluble T*t*BT–butanediol compound corresponded to a composition of 3

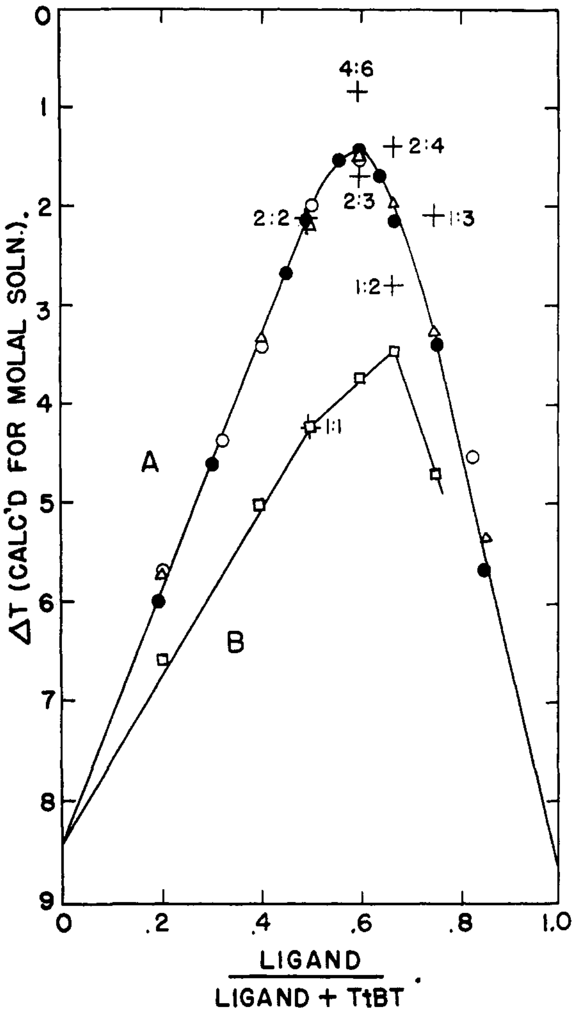
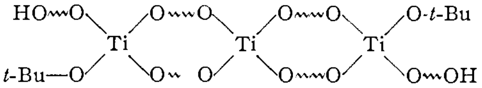


Fig. 2.—The freezing point depressions of solutions containing a total of one mole of solute (ligand plus T*t*BT) per 1000 g. of *t*-butyl alcohol. The plus signs indicate values calculated for various titanate:ligand compounds. A, glycol ligands: ●, ethylene glycol; ○, butanediol; △, octylene glycol. B, ethyl acetoacetate ligand.

atoms of titanium, 6 moles of butanediol and 2 moles of *t*-butyl alcohol less 12 hydrogen atoms. The observed molecular weight in benzene was low, but probably as close to the calculated value as can be expected in view of the observed instability of the compound in benzene. The molecular weight was definitely greater than required for a molecule containing only two titanium atoms. Structure V is tentatively assigned to the new compound. The wavy lines in V represent the hydrocarbon skeletons of butanediol.



V

The results obtained with three simple glycols are not in accord with expectations based upon structures I to IV. Instead of reacting in a simple 1:2 ratio, T*t*BT with bidentate glycol ligands appears to build up larger molecular aggregates.

The compositions of these aggregates are indicated by the plus signs of Fig. 2. These points represent the calculated freezing point depressions for various titanate:ligand compounds. In making these calculations K_f was assumed to be 8.4 for the various compounds.

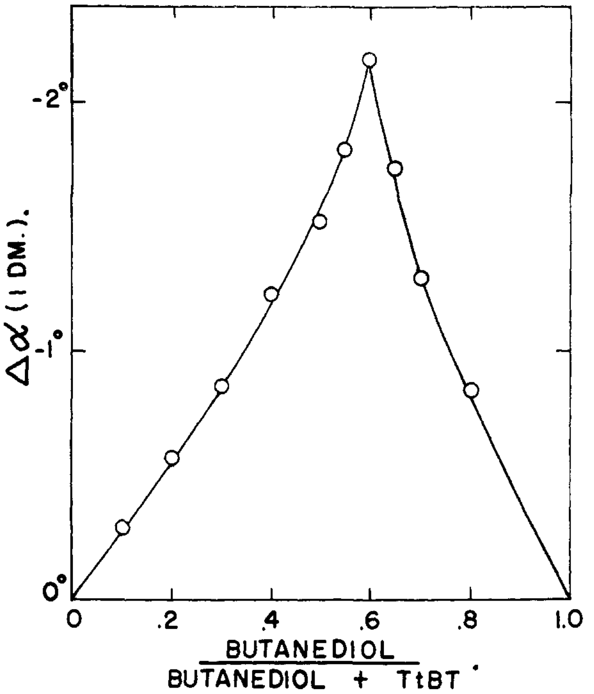
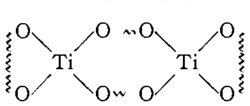


Fig. 3.—Changes in optical rotation due to complexing in *t*-butyl alcohol solutions containing T*t*BT and D-(−)-butanediol-2.3. Total molarity, T*t*BT plus butanediol, 0.439 mole per 1000 ml. of solution.

Consideration of curve A (Fig. 2), representing the T*t*BT–glycol reaction leads to the conclusion that a curve having this shape and position could not result from a single compound. Titanium: glycol compositions of 1:1, 1:2 and 1:3 appear to be unlikely, but four possible compositions remain, namely, 2:2, 2:3, 2:4 and 4:6. Curve A passes directly through the point calculated for a 2:2 compound. It reaches its peak at a point definitely above that calculated for the 2:3 compound, a result which requires the existence of a still larger aggregate in the solution. The curve then passes below the position calculated for the 2:4 compound, but well above that calculated for the 1:2 compound. Proceeding from the right-hand side of the figure the curve appears to start in the direction of the 2:4 complex and to fall off slightly as the mole fraction of ligand becomes less, due possibly to the formation of some 2:3 compound. As the concentration of 2:3 compound becomes great (at mole fraction 0.60) some may dimerize to the 4:6 compound.

The only insoluble compound isolated during this work was a T*t*BT–butanediol compound containing, apparently, three atoms of titanium and six molecules of butanediol, and two molecules of *t*-butyl alcohol. In the region where this compound formed the freezing points of the T*t*BT–butanediol solutions diverged markedly from curve A, and in the direction indicative of larger molecular aggregates. It is believed that ethylene glycol and octylene glycol have a greater tendency to chelate with titanate (and thus to terminate the polymerization) than has butanediol. Although ethylene glycol and octylene glycol apparently do not form structures like III or IV, they may partially chelate to form structures like VI.



VI

Butanediol, being less able to chelate, builds up the larger, insoluble compound V.

The experiments with ethyl acetoacetate (Fig. 2, curve B) show exactly the type of behavior expected for T*t*BT–ligand compositions of 1:1 and 1:2. These experiments support Schmidt's structure IV. Working with the *n*-butyl titanate Schmidt[3] showed that two butyl groups remained in the 1:2 compound. It is not indicated whether or not two *t*-butyl groups remain in the present instance, but some compound containing one T*t*BT and two ethyl acetoacetate molecules must exist.

The present findings do not exclude the possibility of cellulose or cellulose derivatives reacting with titanates to form structures similar to I or II. In cellulose the hydroxyl groups being located on pyranoside rings may have altered reactivity because of their relatively fixed position. Further studies with cyclic glycol derivatives will be required to illuminate this point.

Acknowledgment.—The micro carbon and hydrogen analyses were performed by Lawrence E. Brown, and Frank C. Magne assisted in the purification of the *t*-butyl alcohol.

NEW ORLEANS, LA.