

electronegativity of the oxygen in triethyloxonium fluoroborate is much larger than in the etherate, as would be expected.

A more subtle indication that this method applies to triply attached oxygen, as well as doubly attached, comes from the difference in apparent electronegativity of the oxygen in aluminum and gallium triethyl etherates. Since the aluminum is less electronegative, it would coordinate more strongly with the oxygen of the ether which would in turn have a higher apparent electronegativity than in triethylgallium etherate. It is indeed found that the apparent electronegativity of the oxygen in triethylaluminum etherate is greater.

No agreement was found between the spin cou-

pling of the methyl and methylene protons and the electronegativity of the substituent attached to the ethyl group. This makes the validity of the equation relating them rather doubtful.⁴

Conclusion

Proton magnetic resonance spectra show that the electron withdrawing power of an element is reduced when it coordinates with an electron donor. It is also confirmed that the electronegativity of gallium is greater than that of aluminum.

Acknowledgments.—We are indebted to the National Science Foundation for support in part of this work.

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[CONTRIBUTION FROM THE PIGMENTS DEPARTMENT, E. I. DU PONT DE NEMOURS & CO.]

Interaction of Tetraisopropyl Titanate and Monoethylamine in *n*-Decane Solution

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RECEIVED MARCH 16, 1959

The interaction of tetraisopropyl titanate (TPT) and monoethylamine has been studied at 25 and 35° in *n*-decane solution and has been found to be weaker than previously-reported interactions between amines and titanium chlorides.

Stable donor-acceptor bonds can be formed between basic nitrogen compounds and titanium(IV) and titanium(III) chlorides. Antler and Laubengayer¹ have shown that trimethylamine reacts with TiCl₄ and TiCl₃ to form the addition compounds TiCl₄·(Me)₃N and TiCl₃·2(Me)₃N. These compounds, in which the titanium shows an apparent coordination number of five, are crystalline solids which can be sublimed *in vacuo* without decomposition. Emel us and Rao² have recently reported the six-coordinated addition compounds TiCl₄·2Py, TiCl₄·2CH₃CN and TiCl₄·2(C₆H₅)CN. The enthalpy of formation of the solid TiCl₄·2Py complex from TiCl₄ and pyridine was reported to be -28 kcal./mole.

Molecular association, presumably resulting from formation of Ti-O(R)·Ti coordinate oxygen bridges, has been observed for the *n*-alkyl titanates up to *n*-hexyl³⁻⁵. With the *sec*-alkyl and *t*-alkyl titanates, on the other hand, molecular association is blocked by the steric effects of the groups adjacent to the bridging oxygens, and these titanium esters have been found to be essentially monomeric.^{6,7}

Little has been published about the existence or stability of complexes between nitrogen com-

pounds and titanium alkoxides. Schmitz-DuMont⁸ has reported that the compound K₂[Ti-(OMe)₄(NH₂)₂] is obtained by reaction of tetramethyl titanate with potassium amide. Reaction between tetraisopropyl titanate (TPT) and monoethylamine to yield a solid 1:1 addition compound has been observed by Gulledge,⁹ who crystallized the compound TPT·EtNH₂ at room temperatures from concentrated mixtures of the titanium ester and excess amine in cyclohexane. A preliminary X-ray study by Gulledge of the TPT·EtNH₂ crystals indicated a hexagonal structure with four molecules in a unit cell of dimension *a*₀ = 10.41 Å, *c*₀ = 22.25 Å. At room temperature in the absence of excess monoethylamine TPT·EtNH₂ underwent slow dissociation with evolution of the volatile amine.

Experimental

Materials.—Tetraisopropyl titanate was distilled at reduced pressure through a 16" Vigreux column. The center cut (b.p. 79.0° at 2.50 mm.) was stored in the dark under nitrogen.

Monoethylamine was fractionated in a 1 × 30" vacuum jacketed column packed with 3/16" Fenske helices and was subsequently sealed under vacuum in Pyrex ampoules one end of which had been drawn out to form a capillary break-off tip. As a test of purity, four ampoules chosen at random were broken under standard HCl and the neutralization equivalent was measured. The observed neutralization equivalent was 45.05 ± 0.4; calcd. for EtNH₂, 45.08.

n-Decane was dried by refluxing over sodium metal and fractionated through the previously-described one inch diameter column. The distillate boiling between 174.2-174.6° at 767 mm. was retained and stored under nitrogen. Samples were periodically analyzed for water by the Karl Fischer procedure. Found: 0-0.05 g. H₂O/l.

Benzene (reagent grade) was dried over sodium and used without further purification.

Cryoscopic Measurements.—Measurements of the freezing point depression of benzene by TPT were made under a

(1) M. Antler and A. W. Laubengayer, *THIS JOURNAL*, **77**, 5250 (1955).

(2) H. J. Emel us and G. S. Rao, *J. Chem. Soc.*, 4245 (1958).

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

(4) C. N. Caughlan, H. S. Smith, W. Katz, W. Hodgson and R. W. Crowe, *THIS JOURNAL*, **73**, 5652 (1951).

(5) (a) D. C. Bradley, R. C. Mehrotra and W. Wardlaw, *J. Chem. Soc.*, 2027 (1952); (b) D. C. Bradley, R. C. Mehrotra, J. D. Swanwick and W. Wardlaw, *ibid.*, 2027 (1953).

(6) D. C. Bradley, R. C. Mehrotra and W. Wardlaw, *ibid.*, 4204, 5020 (1952).

(7) Bradley, *et al.* (reference 6, p. 4204), report an average molecular association of 1.4 for TPT. Steric hindrance makes establishment of a Ti-O(i-Pr)-Ti bond unlikely; also the cryoscopic molecular weight determinations reported below indicate TPT to be monomeric.

(8) O. Schmitz-DuMont, *Angew. Chem.*, **62**, 560 (1950).

(9) H. C. Gulledge, private communication.

N_2 atmosphere in a jacketed tube containing a Beckmann thermometer and a mechanical stirrer. Cooling curves were run for 25-cc. samples of pure benzene and for benzene containing 1- and 2-cc. portions of TPT. The apparent TPT molality m was related to the observed freezing point depression ΔT by the expression $\Delta T = 5.12m$. The apparent molecular weight of TPT in 0.15 m solution was 283.5 (two determinations); the apparent molecular weight of TPT in 0.31 m solution was 282.2 (three determinations); calcd. for TPT monomer: 284.2.

As a check upon the accuracy of this procedure, the molecular weight of benzil was determined in a manner similar to that employed for TPT. Found: 209; calcd., 210.2.

Ethylamine Activity as a Function of TPT and $EtNH_2$ Concentrations.—TPT and n -decane were contained in a round bottomed flask to which was connected, through mercury-sealed ground joints, a manometer and a bulb containing four weighed $EtNH_2$ ampoules. This assembly was evacuated to the vapor pressure of the decane-TPT solution, sealed off, and the flask and manometer portion of the apparatus immersed in a well-stirred water-bath constant to $\pm 0.05^\circ$. Before addition of ethylamine the solution was stirred with a "Kel-F" covered magnetic stirrer bar for several hours to ensure thermal equilibrium and to test the system for slow leaks or inadequate outgassing of the decane-TPT solution.

The ethylamine was introduced into the vapor space above the stirred solution by twisting a stopcock which broke the capillary tip of an ampoule. An immediate pressure rise was observed, followed by a fairly rapid (90% in *ca.* 10 min.) approach to an equilibrium pressure. Final pressure readings were taken after the observed pressure was constant with time. The total amounts of ethylamine contained in the system after release from the ampoules were determined from the differences in weight between the filled and empty ampoules.

The internal pressures, as registered by the Hg manometer attached to the apparatus, were read with a cathetometer. The ethylamine vapor pressures above the solutions were taken to be equal to the observed internal pressures minus a small and nearly constant correction of about 2 mm. for the vapor pressure of the solvent.

Experimental error was introduced into these measurements by traces of moisture entering the system during its assembly or with n -decane. There was also difficulty in complete recovery of the capillary tips of the broken ampoules. The over-all uncertainty in the $EtNH_2$ pressure-concentration results from these sources is estimated at approximately 6%.

Results and Discussion

Monoethylamine vapor pressures above solutions of 0.01–0.12 mole fraction $EtNH_2$ in n -decane were determined at 20, 25, 30 and 35° . From the resulting pressure-concentration data the activity coefficients of $EtNH_2$ in n -decane, $\gamma_{EtNH_2} = P_{EtNH_2} / X_{EtNH_2} P^0_{EtNH_2}$, were calculated.¹⁰ The data of Fig. 1 show that γ_{EtNH_2} is larger than unity and decreases with increasing X_{EtNH_2} and with temperature. This non-ideal behavior of the $EtNH_2$ - n -decane system is presumably the result of the difference in polarity of the two components.

Figure 2 records the monoethylamine pressure-concentration behavior observed at 25° with solutions of initial TPT concentrations $X_{TPT} = 0.012$ and 0.060 mole fraction. This figure shows that addition of 6 mole % of TPT to the n -decane solvent reduces by approximately 40% the apparent activity coefficient of the monoethylamine.

A decrease in amine activity of this magnitude can in principle be due to changes in the physical nature of the solvent that are produced by addition of the relatively polar ester. Some insight into the magnitude of this effect of solvent polarity

(10) Values of $P^0_{EtNH_2}$ at 20, 25, 30 and 35° were calculated from the data compiled by R. R. Dreisbach as Serial N. 16-5 in "Physical Properties of Chemical Substances," The Dow Chemical Co.

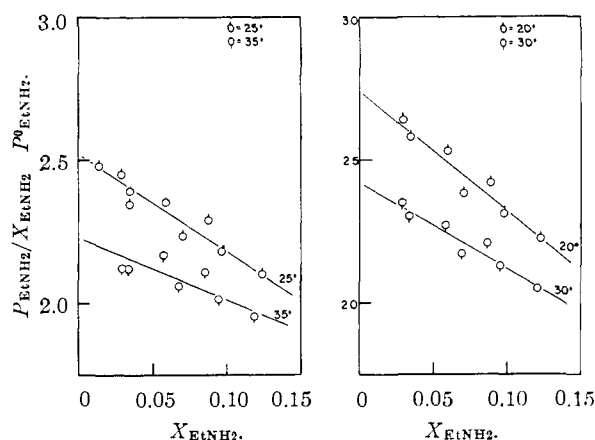


Fig. 1.—Activity coefficient of ethylamine vs. concentration in n -decane solution.

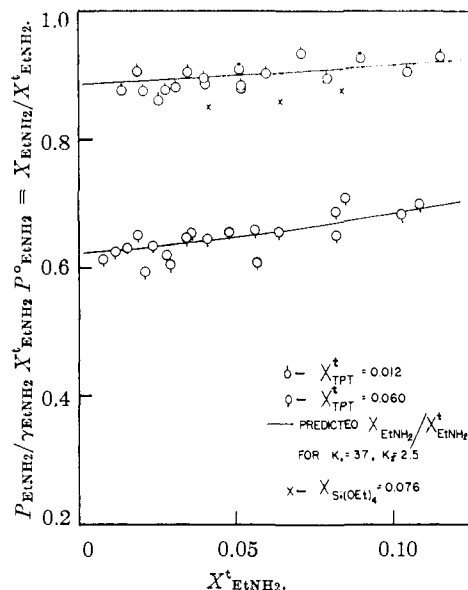
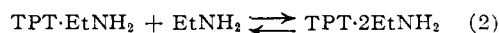
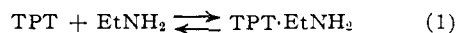


Fig. 2.—The apparent fraction of the total ethylamine present as free ethylamine vs. total ethylamine concentration in n -decane + TPT solutions at 25° .

upon $EtNH_2$ activity coefficient can be obtained from the behavior of $EtNH_2$ in n -decane solutions of tetraethyl orthosilicate. The silicate ester resembles the titanium ester in polarity and should change the structure of the n -decane solvent in a similar manner, while reduction of $EtNH_2$ activity by formation of coordination compounds is unlikely. The data for solutions of $EtNH_2$ in n -decane containing 7.6 mole % of $Si(OEt)_4$ are presented as the crosses in Fig. 2; the activity of $EtNH_2$ is reduced by <15% by the presence of this concentration of silicate ester.

The reduction of $EtNH_2$ activity in TPT-containing solutions alternatively can be regarded as resulting from the amine-titanate complexing equilibria



The experimentally observed vapor pressure vs. composition behavior of the ethylamine and ti-

tanium ester solution is consistent with the existence of two equilibrium constants

$$K_1 = \frac{X_{TPT \cdot EtNH_2}}{X_{TPT} X_{EtNH_2}} \frac{X_{EtNH_2}}{X_{EtNH_2}}$$

$$K_2 = \frac{X_{TPT \cdot 2EtNH_2}}{X_{TPT} X_{EtNH_2}^2} \frac{X_{EtNH_2}}{X_{EtNH_2}}$$

The solid curves on Fig. 2 represent that variation of $\frac{p_{EtNH_2}}{p_{EtNH_2}^0} \frac{X_{EtNH_2}}{X_{EtNH_2}^0}$ with $EtNH_2$ concentration to be expected from (1) and (2) for the case where $K_1 = 3.7$ and $K_2 = 2.5$. Behavior observed at 35° can again be accounted for by (1) and (2), with the best fit of the data being given by $K_1 \sim 3.4$, $K_2 \sim 2.3$. Less satisfactory fits of the data are obtained by assuming that the complexing of $EtNH_2$ is accomplished solely by (1) or (2).

The magnitudes of the constants K_1 and K_2 indicate that the coordination compounds $TPT \cdot EtNH_2$ and $TPT \cdot 2EtNH_2$, if indeed they exist in solution, have only a low stability. Application of the van't Hoff equation to these K 's at 25 and 35° indicates that the enthalpy change for (1) and (2) is < -2 kcal.

The weakness of the TPT-ethylamine interaction was unexpected in view of the relatively high stability of the reported $TiCl_4$ -amine compounds. The comparative stabilities of the TPT and $TiCl_4$ complexes possibly reflect the relative abilities of the isopropoxide and the chloride groups to supply electrons to the Ti(IV) atoms to which they are bonded. Alkoxide groups, being less electronegative than chlorides, should behave as more effective electron donors to the vacant orbitals of the Ti(IV) atoms and accordingly Ti(IV) alkoxides might be anticipated to act as weaker Lewis acids than $TiCl_4$.

Although isopropoxy groups are more bulky than are chlorides, the formation of TPT-ethylamine complexes is not precluded by steric effects. This can be demonstrated by construction of a Fisher-Hirschfelder scale model of octahedral $TPT \cdot 2EtNH_2$. $EtNH_2$ groups are observed to fit into such a structure without strain.

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[CONTRIBUTION FROM THE CHEMICAL AND METALLURGICAL DIVISION, SYLVANIA ELECTRIC PRODUCTS, INC.]

Preparation, Properties and Structure of Cadmium Peroxide

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RECEIVED DECEMBER 15, 1958

A compound shown to be CdO_2 has been prepared and some of its properties are given. The crystal structure of this material has been studied by powder diffraction methods. Patterns were indexed on the basis of a cubic pyrites-type lattice with the cadmium atoms occupying the fcc positions. A value for a_0 of 5.313 ± 0.003 Å, and an oxygen-oxygen peroxide distance of 1.49 ± 0.04 Å, were found.

Introduction

True peroxides, containing the $-O-O-$ linkage, of the type M_2O_2 and MO_2 , of the alkali and alkaline earth elements, respectively, are comparatively well-known and their crystal structures have been established. Extensive references easily may be found in standard inorganic reference books such as Mellor's treatise.¹ Recently Föppl² has published a comprehensive paper on the preparation and structure of the alkali, or Group Ia, peroxides. Föppl discusses the $-O-O-$ linkage and includes a survey of the currently known structures of inorganic peroxides. Significantly, his summary includes only the alkali peroxides, hydrogen peroxide, the peroxides of Ca, Sr and Ba, and the octahydrates of these Group IIa peroxides.

Group Ib and IIb peroxides (along with the peroxides of Be and Mg), on the other hand, do not form easily defined chemical species. The difficulty in preparation and the instability of these peroxides is attributed to the lower electropositive nature of the Group IIb metals as compared to Ia and IIa. No structural studies on the Group Ib or IIb peroxides have been made.

There are several general methods employed to prepare peroxides. Often the direct reaction of oxygen with the metal in air (or oxygen) and in liquid ammonia may be employed. Another com-

mon method is the reaction of a metal salt, usually in basic solution, with hydrogen peroxide. In addition to these preparations, thermal decomposition of the superoxides may yield the peroxides and a recent paper³ describes the reactions of various metal salts with alkali superoxides in liquid ammonia to obtain certain peroxides.

Cadmium peroxide of doubtful purity has been reportedly prepared by all of these methods except by the decomposition of a definitely established superoxide of cadmium. Manchot⁴ reported that the low-temperature oxidation of cadmium produced some CdO_2 . Teletof,⁵ and later Perkins,⁶ utilized hydrogen peroxide to prepare materials which probably were fairly pure CdO_2 . Perkins, in addition, also tried to prepare this peroxide from cadmium dimethyl in ethereal solution with hydrogen peroxide. Perkins' work is the most recent and authoritative discussion of this method. He gives, in addition, references to earlier inconclusive CdO_2 preparations. However, Perkins, largely because he depended upon chemical evidence alone, was unable to establish definitely the presence of CdO_2 . Recently, Schechter and Kleinberg³ claimed a reaction product rich in the corresponding peroxide upon treating cadmium salts in liquid ammonia with alkali superoxides.

(3) D. L. Schechter and J. Kleinberg, *THIS JOURNAL*, **74**, 3297 (1954).

(4) W. Manchot, *Ber.*, **42**, 3942 (1909).

(1) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1922.

(2) H. Föppl, *Z. anorg. allgem. Chem.*, **291**, 12 (1957).

(5) I. S. Teletof, *J. Russ. Phys. Chem. Soc.*, **43**, 131 (1911).

(6) T. R. Perkins, *J. Chem. Soc.*, 1687 (1929).