refractive index corresponds with that of a mixture containing 51.1% α-pinene.

The mixture, 2.05 g., was treated with silver perchlorate, 0.75 g., and left to stand at 25° for 7 hr., when the products were separated by the method described above. The liquid, 1.00 g. (49%), distilled from the mixture had $\alpha^{25}D$ +30.7°, $n^{25}D$ 1.4662. These figures correspond with those of a mixture of α-pinene with β-pinene containing 78.3 and 78.2% α-pinene, respectively. The liquid, 0.60 g. (29%), obtained by treating the solid phase with water, 2 ml., had $\alpha^{25}D$ −14.7°, $n^{25}D$ 1.4756. These figures correspond with those of a mixture containing 92.2 and 93.1% β-pinene, respectively. The agreement between the two methods of analysis for both fractions confirms that no chemical change had occurred and that the recovered liquids consisted of only the mixed pinenes.

Behavior of α-Pinene and β-Pinene toward Aqueous Silver Perchlorate.—A solution of silver perchlorate, 6 g., in water, 5 ml., was shaken with β-pinene, 0.5 ml., for several minutes at 25°. The β-pinene was thereby completely converted to a white solid, which was not analyzed but was probably the same complex as that formed in the absence of water. An identical experiment in which α-pinene was substituted for the β-pinene did not produce any solid, the α-pinene remaining instead as a separate liquid phase. A further experiment, in which a mixture, 0.5 ml., of equal volumes of the two pinenes was taken, gave a mixture of solid and two liquid phases. This might be a promising method for the separation of α-pinene and β-pinene from each other.

Preparation of Silver Nitrate–Cyclohexene Complex.[15]—Silver nitrate, 3.6 g., was dissolved in a warm mixture of cyclohexene, 15 ml., and ethanol, 2 ml. At room temperature a system of two colorless phases was formed, and at 0° the lower phase gave a mass of needle-shaped crystals. Filtration at *ca.* 4° gave 4.6 g. of product, m.p. 24–32°.

Anal. Calcd. for $AgNO_3 \cdot 2C_6H_{10}$: Ag, 32.3. Found: Ag, 33.2, 33.3.

Pinenes and Silver Nitrate.—Attempts to obtain a solid complex were unsuccessful with pinene (practical) or pinene diluted with a solvent, for example, acetone, methanol or ethanol.

Miscellaneous Observations.—Silver perchlorate dissolves readily in 2-pentene, in 1-hexene and in 4-methyl-2-pentene to form systems consisting of two colorless liquid phases.[16] Crystals form when the 2-pentene system is cooled below room temperature. Silver nitrate dissolves to some extent in 2-pentene and in 4-methyl-2-pentene, but no second liquid phase results.

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[15] The complex, but not its preparation, has previously been described by Salomon.[6]

[16] Francis[7] found that silver nitrate gave two liquid phases with propene and 1-butene but not with mixed pentenes.

PASADENA, CALIF.

[CONTRIBUTION NO. 2191 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Coördination of Silver Ion with Unsaturated Compounds. X. Complexes of Silver Perchlorate and Silver Nitrate with Alkynes[1]

BY ALAN E. COMYNS[2] AND HOWARD J. LUCAS[3]

RECEIVED MARCH 6, 1957

Systems of silver nitrate and silver perchlorate with 2-butyne, 2-pentyne and 3-hexyne have been studied. Solid complexes are formed, and their solubilities in the alkynes have been measured at 25°.

Previous investigations in this series[4,5] of the coördination[6] of alkynes with silver ion were devoted to measuring equilibrium constants in aqueous solution. We now report studies on systems formed in the absence of added solvent. As before, only dialkylacetylenes have been studied in order to obviate complications from the presence of acidic hydrogen atoms on 1-alkynes.

Silver perchlorate and silver nitrate differ markedly in their solubilities in the three alkynes, as shown in Table I. Except in the case of the silver perchlorate–2–butyne system, where a solid complex is rapidly and quantitatively formed, the solids in contact with the "saturated" solutions were mixtures of unreacted silver salt with solid complexes. This was due to the slowness with which solid complexes were formed, and in consequence the solubilities given in Table I are not true equilibrium values.

TABLE I

SOLUBILITIES OF $AgClO_4$ AND $AgNO_3$ COMPLEXES IN ALKYNES AT 25°

	2-Butyne	2-Pentyne	3-Hexyne
$AgClO_4$[a]	0.10	68	65
$AgClO_4$[b]	.10	211	185
$AgNO_3$[a]	.28	0.22	0.24

[a] Grams of $AgClO_4$ or $AgNO_3$ per 100 g. of solution.
[b] Grams of $AgClO_4$ per 100 g. of solvent.

Silver Perchlorate Complexes.—The solubility of silver perchlorate in 2-pentyne and 3-hexyne is about two thousand times that in 2-butyne. This is probably a consequence of the symmetry of the 2-butyne molecule, which favors packing into a crystal lattice, rather than the formation of concentrated solutions. Similar behavior is found in related systems: thus silver perchlorate is insoluble in dioxane[7] but very soluble in tetrahydropyran[8] and is sparingly soluble in cyclohexene but very soluble in 1-hexene.[9] In each of these systems the solvents of more symmetrical structure readily form solid complexes with silver perchlorate but are poor solvents for these complexes.

The compositions of the "saturated" solutions of silver perchlorate in 2-pentyne and 3-hexyne at 25° correspond with molal ratios of alkyne to silver perchlorate of 1.4:1. Partial evaporation of the

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[1] This research has been made possible by support extended the California Institute of Technology by the Office of Naval Research under Contract Nonr-270(00).

[2] Arthur Amos Noyes Fellow, 1952–1953.

[3] To whom requests for reprints should be sent.

[4] W. S. Dorsey and H. J. Lucas, THIS JOURNAL, **78**, 1665 (1956).

[5] G. K. Helmkamp, F. L. Carter and H. J. Lucas, *ibid.*, **79**, 1306 (1957).

[6] The reaction is considered to be complexing; J. G. Traynham and M. F. Sehnert, *ibid.*, **78**, 4024 (1956).

[7] A. E. Comyns and H. J. Lucas, *ibid.*, **76**, 1019 (1954).

[8] A. E. Comyns and H. J. Lucas, unpublished results.

[9] A. E. Comyns and H. J. Lucas, THIS JOURNAL, **79**, 4339 (1957).

alkyne gives in each case a solid in which this ratio is approximately 1:3.

Solutions of 7.2 to 41% silver perchlorate in 2-pentyne (molal ratios of alkyne to silver perchlorate between 39:1 and 4.3:1) exist at 25° as two conjugate liquid phases of these compositions. Solutions containing less than 7.2% and between 41 and 68% of silver perchlorate in 2-pentyne consist of one liquid phase. The more concentrated solutions are viscous and become pale brown after standing for several days.

Solutions of silver perchlorate in alkynes silver-plate metallic copper, as do solutions of silver salts of fluoro acids in aromatic hydrocarbons.[10] Concentrated solutions in 2-pentyne and 3-hexyne explode on contact with mercury.

Vapor pressure data obtained on the system silver perchlorate–2-butyne, are plotted in Fig. 1. Systems containing 2-butyne in excess of the formula $AgClO_4 \cdot 3C_4H_6$ exert a pressure equal to that of 2-butyne (254 mm. at 0°), and those containing between 3 and 2.5 moles[11] of 2-butyne to 1 of silver perchlorate have a vapor pressure of 46 mm. at 0°.

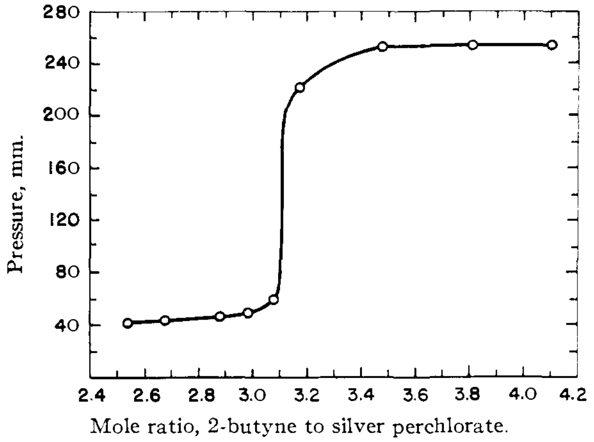

Fig. 1.—Vapor pressure of 2-butyne in the silver perchlorate–2-butyne system.

Silver Nitrate Complexes.—The solubility of silver nitrate is about the same in 2-butyne, 2-pentyne and 3-hexyne (Table I). 2-Pentyne reacts the most rapidly, for within a few minutes of adding powdered silver nitrate a fluffy white powdery complex is noticed. In the presence of a trace of moisture, introduced for example by working in an open test-tube, a second liquid phase forms, but even when the anhydrous reactants are heated to 90° in a sealed tube, no second liquid phase is observed. Evaporation of a saturated solution of silver nitrate gave a small amount of a flaky crystalline solid, $AgNO_3 \cdot 3C_5H_8$. This lost 2-pentyne rapidly on exposure to the atmosphere, and the resulting white powder had the approximate composition $AgNO_3 \cdot C_5H_8$.

When 2-butyne and 2-pentyne were shaken with silver nitrate at 25° for five days, some silver nitrate remained unchanged. 2-Butyne became yellow and a silver mirror was deposited on the walls of the vessel. When a mixture of 2-butyne and silver nitrate was warmed gently to 65°, the crystals of silver nitrate dissolved and a second, denser, initially yellow liquid phase appeared. This rapidly became dark brown and a silver mirror was deposited. Because of this side reaction, no satisfactory complex was isolated.

Powdered silver nitrate reacted quantitatively with 3-hexyne in 8 weeks to give the colorless crystalline complex, $AgNO_3 \cdot C_6H_{10}$.[12]

Experimental

Materials.—Silver perchlorate and silver nitrate were of reagent grade, the former from the G. F. Smith Co. The alkynes were all purchased from the Farchan Research Laboratories and purified by standing over sodium for 24 hr., followed by fractionation through a series of U-tubes in the vacuum system. The purified 2-butyne had v.p. 253 mm. at 0°, in agreement with that calculated from the formula given by Heisig and Davis.[13] The vapor density at 321 mm. and 24.5° was 2.46 g./l., which corresponds to a mol. wt. of 55.2 (calcd., 54.1). 2-Pentyne had $d^{25}{}_4$ 0.705, $n^{25}{}_D$ 1.4005. The vapor pressure of 2-pentyne was measured between −33° and +26° and obeyed the relation $\log_{10} P_{mm} = 8.067 - (1695/T_{abs})$. 3-Hexyne had $n^{25}{}_D$ 1.4091.

Analyses.—The complexes of silver perchlorate with 2-butyne and of silver nitrate with 3-hexyne were analyzed by Dr. A. Elek. Other silver analyses were by thiocyanate titration using ferric alum indicator.

Solubility Measurements.—The solubility measurements for silver perchlorate in 2-pentyne and 3-hexyne are described in their respective sections below. The solubilities of silver perchlorate in 2-butyne and of silver nitrate in 2-butyne, 2-pentyne and 3-hexyne were measured by the following technique. A small quantity of the salt, contained in a glass ampoule fused to the vacuum system, was dried by pumping for at least 24 hr. with a mercury-vapor diffusion pump followed by a liquid-air trap. The alkyne, dried over sodium, was distilled directly into the ampoule which was then sealed off from the vacuum system and left to shake in a thermostat at 25.0° for several days. By this time the silver perchlorate with 2-butyne had been completely converted to a white powder: in the three silver nitrate systems the salt had been partially converted to solid complexes, which had the form of exceedingly thin, transparent flakes. Aliquots of the solutions were transferred to small flasks by pipets which had previously been warmed to 25°. The solutions were evaporated to dryness, and the residues were dissolved in 3 *N* nitric acid and titrated with 0.1 *N* potassium thiocyanate solution.

Silver Perchlorate–2-Butyne.—2-Butyne, 2.8 ml. at 0°, was distilled onto finely crystalline silver perchlorate, 0.90 g., contained in a graduated tube closed by a mercury float valve. In 15 minutes the solid, which had previously occupied 0.6 ml., had become transformed into a white, powdery mass which occupied 2.0 ml. An excess of liquid 2-butyne was present. The solid underwent no further volume change in 15 hr. All volatile constituents were then distilled from the mixture into a trap cooled in liquid air, 2 hr. being required. The distillate consisted of unchanged 2-butyne, 2.8 ml. at 0°, v.p. 254 mm. at 0°. The residual silver perchlorate, now in the form of a fine, white powder, occupied 1.8 ml.; it was completely soluble in water.

The complex was prepared on a sintered-glass disk fused into the middle of a centrifuge tube, the latter initially fused to the vacuum system. After the complex had formed on the disk, the contents of the tube were frozen, and the tube was sealed off from the vacuum system. The excess of liquid 2-butyne was then removed from the solid complex by centrifuging; by this means the solid was in

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[10] D. W. A. Sharp and A. G. Sharpe, *J. Chem. Soc.*, 1858 (1956).

[11] Systems containing less butyne than this were not examined owing to the long time necessary for them to reach equilibrium. The experiment illustrated in Fig. 1 took ten weeks. For this reason it is not possible to deduce the nature of the second solid phase in equilibrium with the complex when less than 3 moles of 2-butyne is present. It may be silver perchlorate or another complex. Solid solutions are precluded by the shape of the vapor pressure curve.

[12] The formation of a solid complex of silver nitrate with 3-hexyne was first observed by F. L. Carter in these Laboratories.

[13] G. B. Heisig and H. M. Davis, THIS JOURNAL, **57**, 339 (1935).

contact with saturated 2-butyne vapor until finally it was removed and sealed in a small glass tube for analysis.

Anal. Calcd. for $AgClO_4{\cdot}3C_4H_6$: C, 39.0; H, 4.91; Cl, 9.59; Ag, 29.2. Found: C, 38.7; H, 5.02; Cl, 8.98; Ag, 29.4.

For the vapor pressure measurements, Fig. 1, silver perchlorate (1.049 g., 0.0051 mole) was contained in a small bulb which was maintained at 0° throughout the experiment. This bulb was connected to a manometer, and, *via* a mercury float valve, to a bulb of known volume, 147 ml., provided with a manometer of known volume per unit length. This larger bulb was in turn connected to the main line of the vacuum system by another mercury float valve. 2-Butyne (1.121 g., 0.0207 mole) was distilled onto the silver perchlorate, the valve was closed, and the mixture was left to equilibrate for 24 hr.; the vapor pressure remained at 254 mm., showing free liquid 2-butyne to have been present. Successive samples of 2-butyne vapor were removed from the small bulb, their masses being determined by measurement of the pressures exerted in the calibrated bulb. The pressures exerted by the complex were recorded as a function of time in order to find when equilibrium was established. Systems in the region of the inflection of the curve, Fig. 1, came to equilibrium in about 2 days, but the system of composition $AgClO_4{\cdot}2.6C_4H_6$ took approximately 30 days. At the conclusion of the experiment (after 10 weeks) the combined samples of removed vapors, 0.276 g., were shown to consist of pure 2-butyne (v.p. 254 mm. at 0°; v.d. 2.45 g./l.) and to account for 65% of the quantity expected on the basis of the separate pressure measurements. The remainder probably was lost through the stopcock grease of the storage flask during the experiment. At the conclusion of the experiment 1.0 ml. of water was admitted to the complex to release the remaining 2-butyne.[14] The liquids were distilled into a trap on the vacuum line and roughly fractionated by allowing the 2-butyne to distil out of the mixture into a second trap containing sodium. The 2-butyne, 0.451 g. (0.0083 mole), thus obtained had v.p. 254 mm. at 0°.

Silver Perchlorate–2-Pentyne.—Silver perchlorate, 4.75 g., and 2-pentyne, 17 ml., were shaken together in a stoppered test-tube in a thermostat at 25.0° for 24 hr. The solid dissolved, forming approximately equal volumes of two colorless liquid phases. The densities of the phases were determined using a pycnometer of 1.7-ml. volume. The concentrations of silver ion in the two phases were measured by shaking known weights with 3 N nitric acid and titrating with 0.1 N potassium thiocyanate. They are expressed as g. of $AgClO_4$ per 100 g. of solution. The upper phase had $d^{25}{}_4$ 0.752; $AgClO_4$, 7.22, 7.24%. The lower phase had $d^{25}{}_4$ 1.136; $AgClO_4$, 41.1, 41.2%.

The liquids remaining after the measurements had been made were treated with an excess of silver perchlorate, and the mixture was stirred intermittently at 25.0° during 48 hr., using a Trubore stirrer fitted in a test-tube. An orange, viscous solution was formed having $d^{25}{}_4$ 1.748; $AgClO_4$, 67.8, 67.9%. The solid phase filtered from this solution appeared to contain unchanged silver perchlorate, contaminated with a small amount of a dark powder: analyses gave $AgClO_4$, 96.3, 95.7%. The viscous solution was evaporated under vacuum to approximately half-volume and the resulting white powder was filtered off.

Anal. Calcd. for $(AgClO_4)_3{\cdot}C_5H_8$: Ag, 46.9. Found: Ag, 47.7, 46.4, 47.3.

Silver Perchlorate–3-Hexyne.—A mixture of silver perchlorate, 16.1 g., and 3-hexyne, 10 ml., was stirred intermittently for four days at 25.0° using the same apparatus as was used for the system with 2-pentyne. Here also a viscous, orange solution was formed. It had $d^{25}{}_4$ 1.654; $AgClO_4$, 64.8, 64.9%. The solid phase which was filtered from this solution had a pale, creamy color and was more powdery than the silver perchlorate taken initially. Analyses gave $AgClO_4$, 95.9, 95.1%. Partial evaporation of the saturated solution yielded a cream-colored powder which was filtered off and freed from excess of 3-hexyne by exposure in the vacuum system for 4 min.

Anal. Calcd. for $(AgClO_4)_3{\cdot}C_6H_{10}$: Ag, 46.0. Found: Ag, 45.6, 45.7.

Silver Nitrate–2-Butyne.—The solid complex taken for analysis was that removed from a mixture which had been used for a solubility determination. This mixture had been shaken at 25° for 5 days and a pale yellow color had developed in the liquid phase. The solid phase, which was separated from this solution by centrifuging in a stoppered tube fitted with a sintered disk, contained small crystals of unchanged silver nitrate.

Anal. Found: Ag, 41.0, 40.5; ratios of $AgNO_3$ to C_4H_6 calcd. from these figures are 1 to 1.72 and 1.78, resp.

Silver Nitrate–2-Pentyne.—The solid phase formed during a solubility experiment was analyzed; the mixture had been shaken in a sealed tube at 25° for 4 days and had remained colorless.

Anal. Calcd. for $AgNO_3$: Ag, 63.5. Found: Ag, 64.0, 63.1.

The yield of crystals formed by evaporating a saturated solution of silver nitrate in 2-pentyne is very small. An apparatus, Fig. 2, was designed in order to repeat the process any desired number of times on the same mixture. Bulb A, 100 ml., contained silver nitrate. 2-Pentyne was distilled onto it from the vacuum system, after which the stopcock was closed and the apparatus was detached from the system. The apparatus was shaken at room temperature for several hours for solution to occur, and then it was carefully tilted in order to decant the solution into bulb B, also 100 ml. With the apparatus in the vertical position again, bulb A was cooled by solid carbon dioxide thus causing 2-pentyne to distil back into bulb A and, by evaporation, to deposit crystals in bulb B which settled in tube C, 5 cm. × 1 cm. When all the 2-pentyne except that in tube C had distilled, bulb A was warmed to room temperature whereupon the whole process was repeated several times. When sufficient crystals had been formed, air was admitted through the stopcock and tube C was cut off. The contents were rapidly filtered and analyzed.

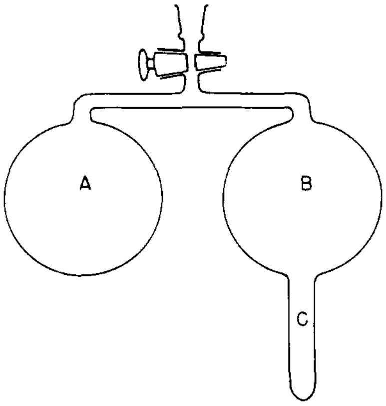

Fig. 2.—Apparatus for the preparation of the silver nitrate-2-pentyne complex.

Anal. Calcd. for $AgNO_3{\cdot}3C_5H_8$: Ag, 28.8. Found: Ag, 30.66, 30.39; ratios of $AgNO_3$ to C_5H_8 calcd. from these figures are 1 to 2.67 and 2.72, resp.

The remainder of the crystals were left in a conical flask, 25 ml., open to the atmosphere, and the rate of loss in weight found, Table II.

TABLE II

CHANGE IN WEIGHT OF $AgNO_3{\cdot}3C_5H_8$ WHEN EXPOSED TO AIR

Time, min.	0	1	2	3	5	9	17	33	46	217
Weight, mg.	70	66	63	61	58	56	53	51	50	50

The very rapid initial loss shows that the samples which had been analyzed must have lost some 2-pentyne prior to analysis, and the initial composition was probably $AgNO_3{\cdot}3C_5H_8$. The powder which had come to constant weight in the atmosphere was analyzed.

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[14] It was later found that distillation into a trap cooled in liquid air would have been more effective.

Anal. Calcd. for $AgNO_3 \cdot C_5H_8$: Ag, 45.3. Found: Ag, 46.5.

Silver Nitrate-3-Hexyne.—A mixture of silver nitrate with an excess of 3-hexyne was prepared following the same technique as in the solubility experiments, and it was left to stand at room temperature for 8 weeks. The tube was then opened and the resulting crystalline mass was freed from liquid by centrifuging in a tube fitted with a sintered-glass disk.

Anal. Calcd. for $AgNO_3 \cdot C_6H_{10}$: C, 28.6; H, 4.00; N, 5.56; Ag, 42.8. Found: C, 28.4; H, 3.92; N, 5.47; Ag, 43.5.

This solid evolved 3-hexyne readily when warmed, and it burned with a smoky flame leaving a residue which contained free silver and also some water-soluble silver compound, presumably silver nitrate.

PASADENA, CALIF.

[CONTRIBUTION FROM THE LABORATORY OF POLYMER CHEMISTRY, TOKYO INSTITUTE OF TECHNOLOGY]

Structures of the Reaction Products of Tetraalkoxytitanium with Acetylacetone and Ethyl Acetoacetate

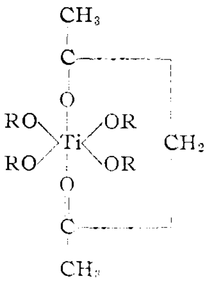
BY AKIO YAMAMOTO AND SHU KAMBARA

RECEIVED APRIL 1, 1957

The structures of the reaction products of a series of tetraalkoxytitaniums with acetylacetone and ethyl acetoacetate were studied by chemical and physical analysis of the isolated pure compounds. In contrast to the previously published paper, penta-coördinated titanium complexes (III and IV) with three alkoxy groups and one bidentate chelating group were obtained when equimolecular proportions of these chelating agents and tetraalkoxytitaniums were used. When two moles of the chelating agents were used per mole of tetraalkoxytitaniums, hexa-coördinated titanium complexes (V and VI) with two alkoxy and two chelating groups were formed. The compounds obtained were found to be present as monomers in dilute benzene solutions. Hydrolysis of dialkoxy-titanium-bis-(acetylacetonate) (V) gave a new type of titanium complex, $[TiO-(CH_3COCHCOCH_3)_2]_2$.

Introduction

Schmidt[1] has studied the reactions of tetraalkoxytitanium (tetraalkyl orthotitanate) with bidentate chelating agents such as diacetone alcohol, acetylacetone and ethyl acetoacetate with the aim of obtaining stable titanic esters. He has proposed the hexa-coördinated structure I for the reaction product of one mole of tetraalkoxytitanium with one mole of acetylacetone and structure II for the product of one mole of tetraalkoxytitanium with two moles of ethyl acetoacetate.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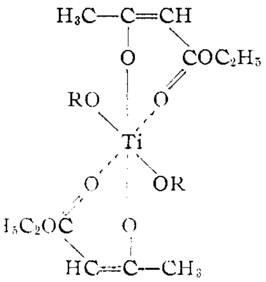
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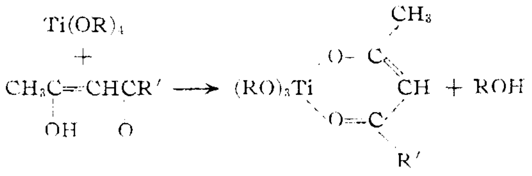
A similar study has been carried out cryoscopically by Reeves and Mazzeno,[2] recently. They have measured the freezing points of *t*-butyl alcohol solutions containing tetra-*t*-butoxytitanium (tetra-*t*-butyl titanate) and ethyl acetoacetate in various ratios and obtained evidence that tetra-*t*-butoxytitanium reacts with ethyl acetoacetate with the formation of 1:1 and 1:2 compounds.

The reaction products have been neither isolated as pure compounds nor analyzed in these two studies. The purpose of the present work was to determine the structures of the reaction products of a series of tetraalkoxytitaniums with bidentate ligands and also to study the physical and chemical properties of the titanium compounds having both alkoxy groups and chelate rings.

Results and Discussions

(a) Reaction of Tetraalkoxytitaniums with Acetylacetone and Ethyl Acetoacetate in a Molar Ratio 1 : 1.—When one mole of acetylacetone was mixed with one mole of tetraalkoxytitaniums (tetraethoxy-, tetrapropoxy- and tetrabutoxy-titanium), crystalline or liquid complex products and one mole of alcohols (ethyl, propyl and butyl alcohol) were obtained. Physical constants and analytical data of the complexes obtained are summarized in Table I (nos. 1, 3 and 5.)

The results of the chemical analyses of the compounds formed lead to structure III, which is considered to be formed by an exchange reaction of an alkoxy group of each tetraalkoxytitanium with bidentate ligand.



III, R′ = CH_3
IV, R′ = OC_2H_5
R = C_2H_5, *n*-C_3H_7, *n*-C_4H_9

A similar experiment on the reaction of tetraalkoxytitanium with ethyl acetoacetate indicated the formation of one mole of trialkoxy-titanium-(ethyl acetoacetate) (IV) (nos. 2, 4 and 6 in Table I) and one mole of alcohols.

These results disagree with Schmidt's proposal for the hexa-coördinated structure I with four alkoxy groups and one chelating group in keto-form bound to central titanium. In order to confirm the structures III and IV, infrared absorption spec-

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[1] F. Schmidt, *Angew. Chem.*, **64**, 536 (1952); German Patent 851,846.

[2] R. E. Reeves and L. W. Mazzeno, Jr., THIS JOURNAL, **76**, 2533 (1954).