

*Anal.* Calcd. for  $\text{AgNO}_3 \cdot \text{C}_5\text{H}_8$ : 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  $\text{AgNO}_3 \cdot \text{C}_6\text{H}_{10}$ : 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.

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

## Structures of the Reaction Products of Tetraalkoxytitanium with Acetylacetonone and Ethyl Acetoacetate

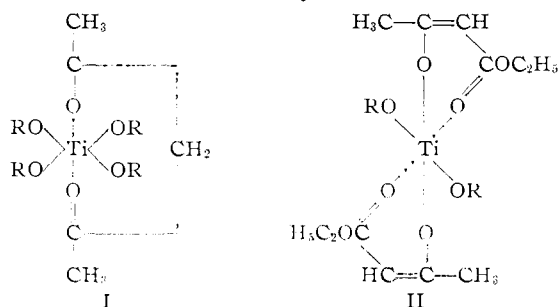
BY AKIO YAMAMOTO AND SHU KAMBARA

RECEIVED APRIL 1, 1957

The structures of the reaction products of a series of tetraalkoxytitaniums with acetylacetonone and ethyl acetoacetate were studied by chemical and physical analysis of the isolated pure compounds. In contrast to the previously published paper, penta-coordinated 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-coordinated 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,  $[\text{TiO}-(\text{CH}_3\text{COCHCOCH}_3)_2]_2$ .

### Introduction

Schmidt<sup>1</sup> has studied the reactions of tetraalkoxytitanium (tetraalkyl orthotitanate) with bidentate chelating agents such as diacetone alcohol, acetylacetonone and ethyl acetoacetate with the aim of obtaining stable titanate esters. He has proposed the hexa-coordinated structure I for the reaction product of one mole of tetraalkoxytitanium with one mole of acetylacetonone and structure II for the product of one mole of tetraalkoxytitanium with two moles of ethyl acetoacetate.



A similar study has been carried out cryoscopically by Reeves and Mazzeno,<sup>2</sup> 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.

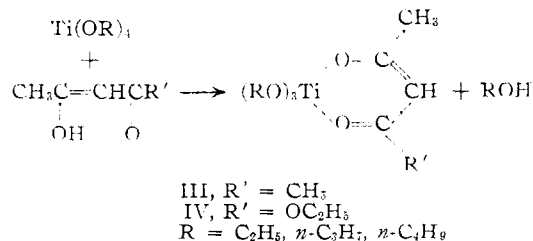
The reaction products have been neither isolated as pure compounds nor analyzed in these two studies. The purpose of the present work was to determine the structures of the reaction products of a series of tetraalkoxytitaniums with bidentate lig-

ands 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 Acetylacetonone and Ethyl Acetoacetate in a Molar Ratio 1:1.**—When one mole of acetylacetonone 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.



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-coordinated 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-

(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).

TABLE I  
 REACTION PRODUCTS IN 1:1 MOLAR RATIO

No.	Formula	Appearance	M.p., °C.	Analyses, %					
				Calcd.			Found		
				Ti	C	H	Ti	C	H
1	(EtO) <sub>2</sub> Ti(acac) <sup>a</sup>	Colorless prisms	59–65 <sup>b</sup>	17.0	46.8	7.86	16.9	45.6	7.72
2	(EtO) <sub>2</sub> Ti(etac) <sup>a</sup>	Colorless prisms	89–92 <sup>b</sup>	15.3	46.2	7.75	15.3	45.6	7.42
3	(PrO) <sub>2</sub> Ti(acac)	Light yell. liquid		14.8	51.9	8.70	14.3	51.4	8.86
4	(PrO) <sub>2</sub> Ti(etac)	Colorless prisms	38–42 <sup>b</sup>	13.5	50.9	8.54	13.6	50.0	8.83
5	(BuO) <sub>2</sub> Ti(acac)	Light yell. liquid		13.1	55.3	10.1	12.9	54.2	8.92
6	(BuO) <sub>2</sub> Ti(etac)	Light yell. liquid		12.1	54.5	9.16	12.2	54.9	8.30

<sup>a</sup> (acac) and (etac) represent chelated acetylacetonate and ethyl acetoacetate groups, respectively. <sup>b</sup> Considerable difficulties were encountered in obtaining sharp melting points on account of the hygroscopic nature of the compounds. Crystals were introduced into a capillary in a dry-box and the melting points were measured after sealing the capillary tube.

 TABLE II  
 REACTION PRODUCTS IN 1:2 MOLAR RATIO

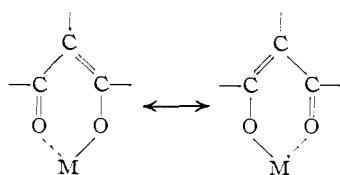
No.	Formula	Appearance	M.p., °C.	<i>d</i> <sup>25</sup> <sub>4</sub>	<i>n</i> <sup>25</sup> <sub>D</sub>	Analyses, %					
						Calcd.			Found		
						Ti	C	H	Ti	C	H
1	(EtO) <sub>2</sub> Ti(acac) <sub>2</sub> <sup>a</sup>	Colorless prisms	48–52			14.3	50.0	7.19	14.2	49.7	7.20
2	(EtO) <sub>2</sub> Ti(etac) <sub>2</sub>	Colorless prisms	40–45			12.1	48.5	7.12	12.1	48.3	7.05
3	(PrO) <sub>2</sub> Ti(acac) <sub>2</sub>	Light yell. liquid		1.125	1.554	13.1	52.8	7.74	13.1	51.8	7.62
4	(PrO) <sub>2</sub> Ti(etac) <sub>2</sub>	Light yell. liquid		1.117	1.526	11.3	50.9	7.60	11.2	51.4	7.23
5	(BuO) <sub>2</sub> Ti(acac) <sub>2</sub>	Light yell. liquid		1.089	1.542	12.2	55.0	8.21	12.1	53.9	9.39
6	(BuO) <sub>2</sub> Ti(etac) <sub>2</sub>	Light yell. liquid		1.090	1.519	10.6	53.1	8.03	10.6	51.8	8.09

<sup>a</sup> See references, Table I.

tra of the products were observed. The results are shown in Fig. 1.

The infrared absorption spectrum of tetrabutoxytitanium (Fig. 1-A) has strong absorption bands at 1080 and 1120 cm.<sup>-1</sup>. Tributoxytitanium-(acetylacetonate) (III) (Fig. 1-B) also has two strong bands at exactly the same positions. The positions of these two peaks agree well with the positions of C–O stretching bands of aliphatic ethers at 1050 and 1150 cm.<sup>-1</sup>. No band was found in the same range of the spectrum of the hydrolysis product of dialkoxy-titanium-bis-(acetylacetonate) (Fig. 1-D), which was prepared by hydrolysis of alkoxy groups of dialkoxytitanium-bis-(acetylacetonate) as is described later. These facts prove that the strong bands are due to C–O stretching vibrations of alkoxy groups bound to a titanium atom.

The spectrum of III (Fig. 1-B) indicates two strong bands at 1376 and 1577 cm.<sup>-1</sup> with nearly equal intensity and a strong band at 1523 cm.<sup>-1</sup>. On the other hand, there is no band observed in the region of unperturbed carbonyl vibrations between 1700 and 1750 cm.<sup>-1</sup>. These results agree well with the results of Lecomte<sup>3</sup> and Bellamy, *et al.*,<sup>4</sup> who have observed two strong bands of nearly equal intensity near 1560 cm.<sup>-1</sup> and between 1310 and 1410 cm.<sup>-1</sup> in the spectra of various metal chelate compounds of acetylacetonate. They have assigned these bands to the asymmetric and symmetric vibrations of two CO links in the resonating structure as



(3) J. Lecomte, *Disc. Faraday Soc.*, **9**, 125 (1950).

(4) L. J. Bellamy and L. Beecher, *J. Chem. Soc.*, 4489 (1954).

The other strong band in the region between 1500 and 1534 cm.<sup>-1</sup> has been assigned by Lecomte to the vibration of perturbed C=C bonds of the enolic form.

The absorption spectrum of tributoxy-titanium-(ethyl acetoacetate) (IV) (Fig. 1-C) is similar to that of tributoxytitanium-(acetylacetonate) (III) (Fig. 1-B), except that the band at 1577 cm.<sup>-1</sup> of acetylacetonate chelate is shifted to higher frequency, 1628 cm.<sup>-1</sup>, in the spectrum of ethyl acetoacetate chelate. The shift is considered to indicate an influence of the substitution of the ethoxy group in place of the methyl group of acetylacetonate. The electron-attracting tendency of the ethoxy group may interfere with the resonance.

Titanium exhibits an apparent coordination number of five in these complexes with three alkoxy groups and one bidentate ligand. However, there exist the alternative possibilities that the compounds may actually be di- or trititanium compounds having the favored coordination number of six. The values of molecular weight determined cryoscopically in benzene solutions are shown in Table III. The observed values roughly correspond to monomer in the molality range between 0.01 and 0.04 mole per 1000 g. of solvent and tend to increase with the solute concentration, suggesting that association might occur to some extent.

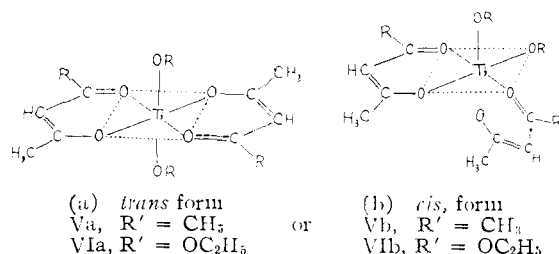
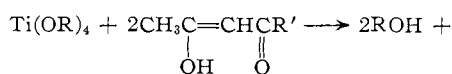
(b) **Reaction of Tetraalkoxytitaniums with Acetylacetonate and Ethyl Acetoacetate in a Molar Ratio 1:2.**—In case of the reaction of the series of tetraalkoxytitaniums with acetylacetonate or ethyl acetoacetate in a molar ratio 1:2, crystalline or liquid complex products and two moles of alcohols were formed. Physical constants and analytical data of the complexes formed are listed in Table II, and the molecular weights are summarized in Table III (nos. 1' to 4').

From these results, the reaction is considered to proceed according to the following equation in agreement with Schmidt's proposal, forming hexa-

TABLE III  
 RESULTS OF MOLECULAR WEIGHT DETERMINATION

No.	Formula	Mole/kg. of solvent	$\Delta T$ , °C.	Molecular weight Found	Calcd.
1	(EtO) <sub>3</sub> Ti(acac)	0.0396	0.179	310	282.2
		.151	.502	430	
2	(EtO) <sub>3</sub> Ti(etac)	.0348	.179	310	312.2
		.0371	.181	335	324.3
3	(PrO) <sub>3</sub> Ti(acac)	.0623	.236	440	
		.0887	.306	475	
4	(PrO) <sub>3</sub> Ti(etac)	.0190	.092	375	354.3
5	(BuO) <sub>3</sub> Ti(acac)	.0198	.100	370	366.3
1'	(EtO) <sub>2</sub> Ti(acac) <sub>2</sub>	0.0195	0.119	280	336.2
2'	(EtO) <sub>2</sub> Ti(etac) <sub>2</sub>	.0119	.065	370	396.3
3'	(PrO) <sub>2</sub> Ti(acac) <sub>2</sub>	.0533	.290	340	364.3
4'	(PrO) <sub>2</sub> Ti(etac) <sub>2</sub>	.0448	.253	385	424.4
		.0604	.362	360	

coördinated dialkoxy-titanium-bis-(acetylacetonate) (Va or Vb) or dialkoxy-titanium-bis-(ethyl acetoacetate) (VIa or VIb).



Infrared spectra of these compounds are essentially the same as those of trialkoxy chelate compounds, indicating the presence of alkoxy and chelating groups.

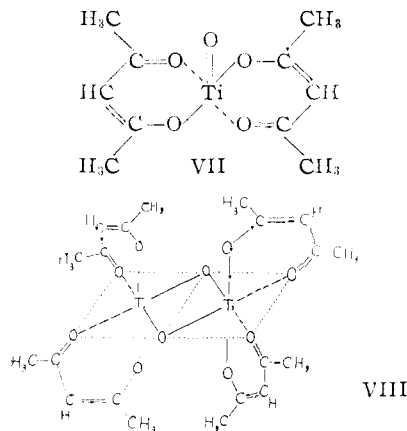
When more than two moles of the chelating agents were used per mole of tetraalkoxytitanium, the same compounds as structure V or VI were obtained. It seems, therefore, that no further substitution of the alkoxy groups with the chelating agents occurs under the condition employed.

**Hydrolyses.**—These complexes (III, IV and VI) with the alkoxy and the chelating groups, except dialkoxy-titanium-bis-(acetylacetonate)s (V), turn to gel-like substances, gradually in moist air and rapidly with the addition of water. The change may be ascribed to the hydrolysis of unstable alkoxy groups and subsequent condensation with the formation of polymeric substances with Ti—O—Ti bonds.

In the cases of diethoxy-, dipropoxy- and dibutoxy-titanium-bis-(acetylacetonate)s, on the other hand, pale yellow needles were produced by addition of water. The crystals were stable in the organic solvents from which the compound was recrystallized. When the solvents were removed, the crystals readily lost their crystalline form.<sup>5</sup> The infrared spectrum of the hydrolysis product of

(5) Similar behavior has been observed by Jones, Pfeiffer and Werner in cases of vanadyl and platinum complexes with acetylacetonate and salicylaldehyde diimine; M. M. Jones, *THIS JOURNAL*, **76**, 5975 (1954); Pfeiffer, *et al.*, *J. prakt. Chem. N. F.*, **149**, 217 (1937); A. Werner, *et al.*, *Ber.*, **34**, 2584 (1901).

V, shown in Fig. 1-D, indicates the complete absence of the absorption bands due to alkoxy groups in the region between 1080 and 1150 cm.<sup>-1</sup>. The other bands due to the chelate rings, near 1370, 1520 and 1570 cm.<sup>-1</sup>, are essentially the same as the bands of dialkoxy-titanium-bis-(acetylacetonate) (V). This fact together with the results of the chemical analyses leads to the formula Ti-(CH<sub>3</sub>COCHCOCH<sub>3</sub>)<sub>2</sub>. Two structures can be considered for this formula, namely, (a) titanyl structure VII and (b) cyclic polymer structure, in which titanium achieves a coördination number of six by the sharing of the oxygen atom between titanium atoms.



Molecular weight determination in benzene solution gave a value of 490, suggesting the dimeric structure VIII, the theoretical value for the monomer being 262.

**Photochemical Reaction.**—The color of titanium acetylacetonates (III, V and VIII) in hermetically sealed glass cells turns to blue when irradiated with a high-pressure mercury lamp or with sunlight. The change in color occurs rapidly in the absence of air, and the development of the blue color is retarded by the air in the cell. When the compounds are exposed to the open air, the blue color disappears rapidly. The blue color could be due to trivalent titanium which is produced by the fission of the Ti—O bond with the action of light. The trivalent titanium thus formed would be oxidized to quadrivalent titanium by oxygen when exposed to the open air. The further investigation of the photochemical reaction will clarify the detailed mechanisms of this reaction.

**Acknowledgment.**—The authors would like to express their sincere thanks to Professor K. Kojima for the infrared spectra and to Professor Y. Inamura for visible and ultraviolet spectra, and to Mr. Y. Takahashi for his assistance. The authors are indebted to the Ministry of Education for financial support.

### Experimental

**Materials.**—Tetraethoxy-, tetra-*n*-propoxy- and tetra-*n*-butoxytitanium were prepared and purified following the method described in the literature.<sup>6</sup> In each case satisfactory purity was indicated by chemical analysis of the compound. Commercially available acetylacetonate and ethyl acetoacetate were purified by fractional distillation and the

(6) J. Nelles, German Patent, 720,080; U. S. Patent, 2,187,821.

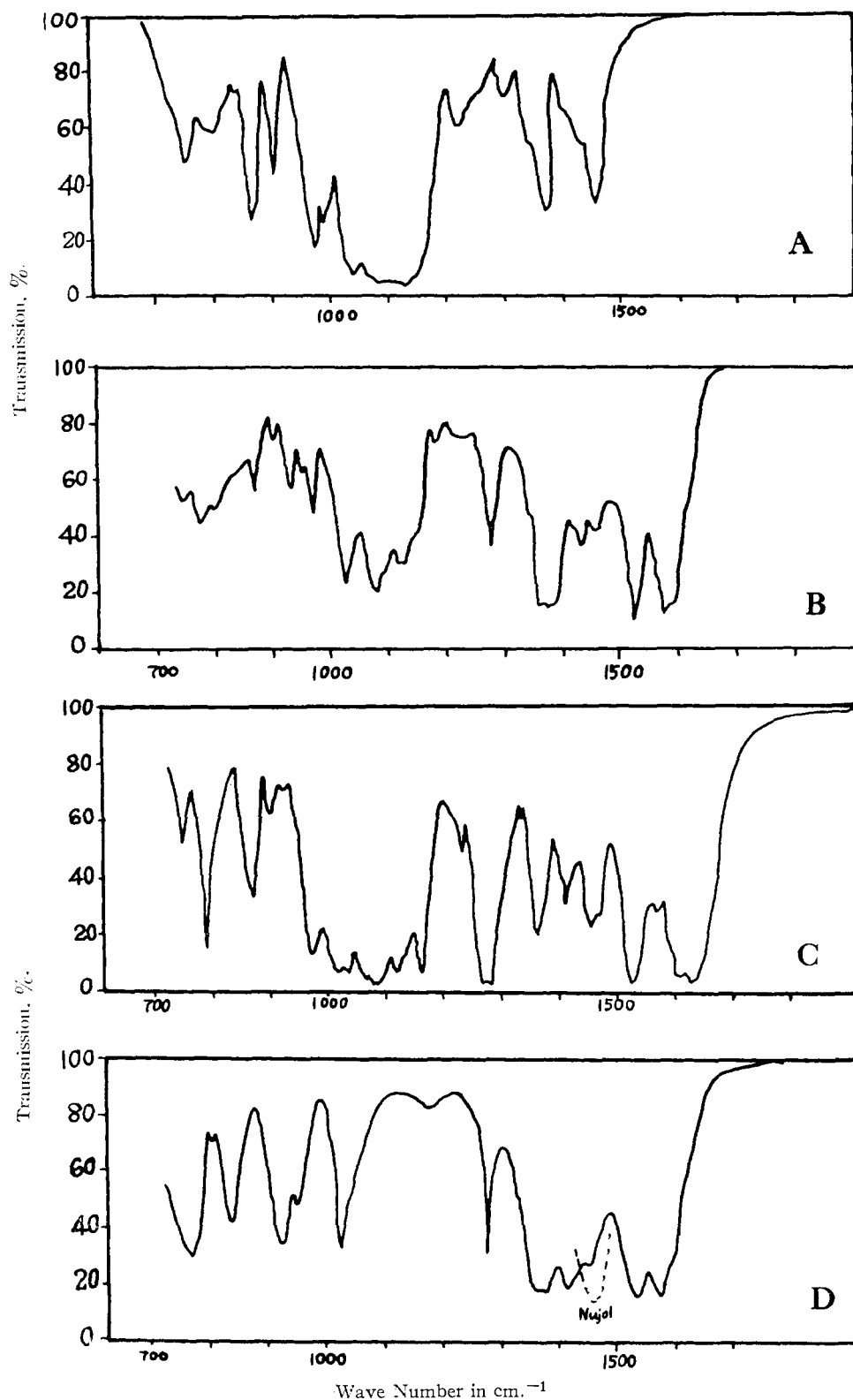


Fig. 1.—Infrared absorption spectra: 1-A,  $\text{Ti}(\text{OC}_4\text{H}_9)_4$ ; 1-B, tributoxy-titanium-(acetylacetonate) (III); 1-C, tributoxy-titanium-(ethylacetoacetate) (IV); 1-D, hydrolysis product of dibutoxy-titanium-bis-(acetylacetonate).

fractions of b.p.  $139\text{--}140^\circ$  (760 mm.) and  $94\text{--}95^\circ$  (40 mm.), respectively, were used;  $n_D^{25}$  for acetylacetonate, 1.4480;  $n_D^{25}$  for ethyl acetoacetate, 1.4169.

General Synthetic Procedures. (a) Reaction of Tetra-

alkoxytitaniums with Acetylacetonate and Ethyl Acetoacetate in a Molar Ratio 1:1.—To 0.010 mole of tetraalkoxytitanium (tetraethoxy-, tetrapropoxy- and tetrabutoxy-titanium) was added 0.010 mole of acetylacetonate or ethyl

acetoacetate. Reaction took place with the evolution of heat and ended within several minutes. The reaction mixture was fractionated under reduced pressure. The volatile liquid distillates were shown to be alcohols by measurements of the refractive indices and boiling points. The quantity of alcohol was 0.010 mole. An equivalent amount (0.010 mole) of compounds III or IV remained as the residue. When the products were solid (see Table I), they were purified using diethyl ether or petroleum ether as solvent. The liquid products were distilled at  $10^{-4}$  mm. with a potstill or "falling-film" type molecular still, maintaining the temperature under  $70^{\circ}$  to prevent heat decomposition. These products are soluble in most organic solvents.

(b) **Reaction of Tetraalkoxytitaniums with Acetylacetonate and Ethyl Acetoacetate in a Molar Ratio 1:2.**—To 0.010 mole of each tetraalkoxytitanium was added 0.020 mole of acetylacetonate or ethyl acetoacetate. Reaction took place with the evolution of heat and ended within several minutes. From the reaction mixtures, 0.020 mole of alcohols were removed under reduced pressure. The theoretical amount (0.010 mole) of compounds V or VI remained as the residue. When the products were solid (see Table II), they were purified using diethyl ether or petroleum ether as solvents. The liquid products were distilled with the molecular still. These compounds are soluble in most organic solvents.

**Molecular Refraction.**—*MR* values for  $(\text{PrO})_2\text{Ti}(\text{acac})_2$ ,  $(\text{PrO})_2\text{Ti}(\text{etac})_2$ ,  $(\text{BuO})_2\text{Ti}(\text{acac})_2$  and  $(\text{BuO})_2\text{Ti}(\text{etac})_2$  were 103.8, 116.6, 113.4 and 125.9, respectively. Since there are no atomic refraction data for hexa-coordinated titanium in the literature, calculation of the molecular refractions was impossible. Instead, the atomic refraction was calculated from observed molecular refractions, and the values of 19.9, 20.1, 20.2 and 20.2, respectively, were obtained for hexa-coordinated titanium from these four *MR* values.

**Hydrolyses of the Compounds and Isolation of VIII.**—The compounds III, IV and VI were hydrolyzed readily by moisture. Gel-like substances were formed after standing several hours in moist air or instantly by addition of water. In case of dialkoxytitanium-bis-(acetylacetonate)s (V), addition of water gave light-yellow needles. To 1.62 g. of  $(\text{BuO})_2\text{Ti}(\text{acac})_2$  was added 5 ml. of water. The crystals obtained were filtered and dried to give 0.74 g. of pale-yellow

amorphous powder. The powder was recrystallized from chloroform or benzene solution, and again light yellow crystals were obtained. The crystals (plate form) were stable in chloroform or benzene solutions, but they lost their crystalline form and turned to a light yellow amorphous substance, gradually in air and rapidly in a vacuum desiccator. The color gradually turned to brown over  $200^{\circ}$  and the compound decomposed to a dark-red liquid at  $235^{\circ}$ .

*Anal.* Calcd. for  $\text{TiC}_{10}\text{H}_{14}\text{O}_6$ : Ti, 18.3; C, 45.9; H, 5.38. Found: Ti, 18.2; C, 45.6; H, 5.57.

Hydrolyses of dipropoxy- and diethoxy-titanium-bis-(acetylacetonate) were carried out analogously with the butoxy-compound, and the products obtained were confirmed to be identical with the hydrolysis product of the dibutoxy-compound by chemical analyses.

The aqueous solution of VIII gave transparent gel-like substance after standing several days at room temperature. When heated over  $40^{\circ}$ , the solution decomposed to an opalescent substance.

**Molecular Weight Determinations.**—Molecular weights were measured cryoscopically in completely dried benzene. The measurements were carried out in a shielded cryoscopic cell with an electromagnetic stirring device after exclusion of air with a stream of dry nitrogen. Freezing points of benzene solutions of some compounds showed a tendency to decrease with time.

**Measurements of Absorption Spectra in the Visible and Ultraviolet Regions.**—Ultraviolet absorption measurements were made with a Beckman DU spectrophotometer using 1.0-cm. silica cells. The absorption spectra of III and V measured in appropriate alcohols showed similar curves having a maximum at  $325 \text{ m}\mu$  ( $\log \epsilon$  3.5). The absorption spectrum of irradiated  $(\text{BuO})_2\text{Ti}(\text{acac})_2$  in the visible region was measured in *n*-hexane and showed a maximum at  $600 \text{ m}\mu$  and a shoulder near  $650 \text{ m}\mu$ .

The infrared absorption measurements were carried out with a Perkin-Elmer recording spectrophotometer model 112. Liquid samples were measured in thin films and the solid sample was measured using Nujol.

TOKYO, JAPAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT DAVIS]

## The Kinetics of Aromatic Hydrocarbon Chlorination in Acetic Acid. The Use of Zinc Chloride as a Catalyst and of Iodobenzene Dichloride as a Halogen Source

BY R. M. KEEFER AND L. J. ANDREWS

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In acetic acid methylbenzenes undergo chlorination by a reaction which is first order in halogen. The reactions are not inhibited by hydrogen chloride and are subject to relatively mild catalysis by zinc chloride. Bromination and iodination reactions in this solvent are of higher order than first in halogen in the absence of catalyst. The reactions are accelerated by zinc chloride and in some cases are complicated by trihalide formation. These differences may be explained in part through consideration of the relative stabilities of trihalide ions in acetic acid and of the role of acetic acid in the substitution reaction. Polymethylbenzenes chlorinate too rapidly in acetic acid for kinetic measurement. To investigate possible steric complications in the reactions of these hydrocarbons, iodobenzene dichloride has been tested as a potentially less reactive chlorinating agent than the free halogens. In this sense it has proved to be unsuitable. It dissociates slowly and comes to equilibrium with its components in dilute solutions in acetic acid. Its rate of reaction with mesitylene and pentamethylbenzene in acetic acid is identical with its rate of dissociation.

The investigation of the relative susceptibilities of a series of polymethylbenzenes to nuclear halogenation with bromine and with iodine monochloride in acetic acid has been simplified by the use of zinc chloride as a catalyst.<sup>1,2</sup> In the presence of this salt the orders of reactions with respect to these halogens reduce to unity and the kinetic complication of trihalide formation<sup>2</sup> is eliminated. In addition, by varying the catalyst concentration, relative halogenation rates for hydrocarbons of

widely different reactivities can be established without changing the halogenating agent. With these observations in mind the effects of zinc chloride on the kinetics of chlorination of various methylbenzenes in acetic acid have been studied, and the results are presented in this paper.

One of the original objectives of this investigation was to determine whether the methyl group steric effect, which so markedly influences the susceptibility of polymethylbenzenes to bromination or iodination,<sup>1,2</sup> is less apparent in chlorination reactions. However, the higher molecular weight hydrocarbons, even in the absence of catalyst, react

(1) L. J. Andrews and R. M. Keefer, *THIS JOURNAL*, **78**, 4549 (1956).

(2) R. M. Keefer and L. J. Andrews, *ibid.*, **78**, 5623 (1956).