BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (7), 1885—1886 (1977)

The Titanium Trichloride-catalyzed Oxidation of Triphenylphosphine with Oxygen in Acetonitrile

Yasuo Chimura and Kimio Tarama

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606

(Received October 29, 1976)

Synopsis. Titanium trichloride catalyzed very rapidly the oxidation of triphenylphosphine with oxygen in acetonitrile, yielding triphenylphosphine oxide and a yellow precipitate. The main catalytic cycle did not contain $Cl_3Ti–O–TiCl_3$ which was produced in the oxidation of $TiCl_3$ alone, but the precursors of $Cl_3Ti–O–TiCl_3$ as intermediates. The yellow precipitate was a titanium(IV) complex with a discrete TiO group.

Titanium(III) complexes are oxidized by molecular oxygen in anhydrous organic solvents to give a μ-peroxo dimeric complex,[1] μ-oxo dimeric complexes,[2,3] or monomeric complexes containing TiO groups.[4] The oxidations of organic compounds with oxygen using titanium complexes as catalysts, however, are unknown. This paper will describe briefly the $TiCl_3$-catalyzed oxidation of triphenylphosphine (PPh_3) with oxygen in acetonitrile as a continuation of previous studies[5] of dioxygen complexes of transition metals.

Experimental

Materials. The acetonitrile was distilled from diphosphorus pentaoxide and again from calcium hydride and then stored under nitrogen. The titanium trichloride was converted to trichlorotris(acetonitrile)titanium(III),[6] which was then dissolved in acetonitrile to yield a 0.130 M solution ($M=mol/dm^3$). The triphenylphosphine was recrystallized from methanol and stored under nitrogen. Commercial oxygen gas was used without further purification.

Apparatus and Procedure. A 200-cm^3, three-necked, flat-bottomed flask containing a Teflon-coated magnetic stirrer was fitted with a thermometer and a serum cap at each of the two necks, while through the other neck it was connected to a vacuum system with a manometer, a gas buret, *etc.* The flask was then immersed in a constant-temperature bath operated at 20 °C. The system was filled with atmospheric oxygen after the introduction of PPh_3 (1.00—8.93 mmol) and acetonitrile (35.0 cm^3). Then, the acetonitrile solution of $TiCl_3$ (5.0 cm^3) was injected as soon as possible by means of a syringe through the serum cap, with vigorous stirring. The uptake of oxygen was followed at the constant pressure of 1 atm. After 2 days, the resulting yellow precipitate was filtered, washed with acetonitrile, and dried under a vacuum. The filtrate was hydrolyzed with dilute hydrochloric acid and extracted with ether. The ether layer was evaporated under a vacuum, leaving a pale yellow residue, which was then chromatographed over silica gel to give PPh_3 and triphenylphosphine oxide ($OPPh_3$).

Spectra. The IR spectra of the yellow precipitate and the reaction solution were measured by means of a JASCO IRA-2 spectrophotometer as Nujol mulls and using a solution cell respectively. The visible spectra of mixtures of $TiCl_3$ and PPh_3 in acetonitrile were recorded under nitrogen with a JASCO UVIDEC-1 spectrophotometer. The ESR spectrum of the precipitate was recorded on a JEOL-JES-3BS-X spectrometer.

Analysis. Carbon, hydrogen, phosphorus, and chlorine analyses of the yellow precipitate were carried out by specialists. The titanium was chelatometrically back-titrated at pH 5.5 with a 0.05 M zinc(II) nitrate solution in 50% aqueous ethanol using Xylenol Orange as an indicator.

Results and Discussion

In the absence of PPh_3, the blue color of an injected $TiCl_3$ solution immediately turned yellow. The uptake of oxygen was very rapid and ceased within a minute. The amount of oxygen taken up was about a fourth of the $TiCl_3$ concentration (Table 1). The IR spectrum of the yellow solution showed a peak at 788 cm^{-1} and a shoulder at 749 cm^{-1}. They were assigned to the stretching vibrations of a Ti–O–Ti group, since $Cl_3Ti–O–TiCl_3(CH_3CN)_4$[7] showed a strong peak and a shoulder at 800 and 740 cm^{-1} respectively. Thus, $TiCl_3$ seems to be oxidized to the same $Cl_3Ti–O–TiCl_3$ complex (**1**) in acetonitrile as in pyridine.[3]

In the presence of PPh_3, an injected $TiCl_3$ solution immediately turned brown, and after several minutes a yellow powder was precipitated. The rate of oxygen uptake was initially very fast, and then it fell rapidly. The amounts of oxygen uptake and of the products formed are shown in Table 1. The ratio of oxygen taken up after 1 min to that after 2 days changed from 0.51 to 0.93 as the amount of PPh_3 decreased. At every stage of the reaction, the amount of oxygen uptake increased with an increase in the amount of PPh_3 and exceeded the amount of $TiCl_3$; that is, the oxidation proceeded catalytically, and the turnover number increased with the increasing amounts of PPh_3. The PPh_3 introduced was recovered almost quantitatively as $OPPh_3$ and unreacted PPh_3. The oxygen taken up was also found almost quantitatively in $OPPh_3$ and in the oxidized catalyst, assuming that the oxidized catalyst bound oxygen in a Ti : O atomic ratio of 2 : 1.

The precipitated yellow complex was air-stable and was hardly soluble in acetonitrile at room temperature. The yield was 33—60%. The complex when recovered from different runs showed the same IR spectra, which contained a strong band at 1146 cm^{-1} and very strong bands at 726 and 1121 cm^{-1} due to the P=O stretching vibration and the X-sensitive vibrations[8] of the coordinating $OPPh_3$ respectively. The spectra also showed a sharp and very strong band at 1060 cm^{-1}, which was assigned to a Ti=O stretching vibration.[4,9] The lack of any absorption between 2000 and 2600 cm^{-1} and between 770 and 960 cm^{-1} indicates the absence of acetonitrile and of a Ti–O–Ti group respectively. The absence of an ESR signal of the complex either at room temperature or at 77 K indicates that the titanium ion is not trivalent but tetravalent. The results of the

Table 1. The amounts of oxygen uptake and products[a)]

Introduced PPh_3 mmol	O_2 Uptake mmol			$2\times O_2$ Uptake mmol (2 day)	Recovered from solution mmol		$OPPh_3$[b)] contained in ppt mmol	Total $OPPh_3$ mmol	Total $OPPh_3$ $+PPh_3$ mmol	Total[c)] O atom in products mmol
	1 min	30 min	2 day		PPh_3	$OPPh_3$				
0	0.17	0.17	—	0.34	—	—	—	—	—	—
1.00	0.62	0.65	0.67	1.34	—[d)]	—[d)]	0.694	—	—	—
2.00	0.80	0.87	1.02	2.04	0.33	0.94	0.666	1.61	1.94	1.94
5.00	0.95	1.30	1.58	3.16	1.93	2.34	0.574	2.91	4.84	3.24
8.93	1.10	1.71	2.16	4.32	4.80	3.60	0.406	4.01	8.81	4.34
3.00[e)]	0.03	0.13	0.66	1.32	1.70	0.65	0.597	1.25	2.95	1.25

a) The amount of $TiCl_3$ was 0.650 mmol. b) Value calculated assuming that $OPPh_3$ is the sole organic component in ppt. c) The Ti : O ratio in an oxidized catalyst was assumed to be 2 : 1. d) They were lost in handling. e) An oxidized $TiCl_3$ solution ($TiCl_3$, 0.650 mmol) was employed as the catalyst.

Table 2. Elemental analyses of the yellow complex

Introduced PPh_3 mmol	%H	%C	%P	%Cl	%Ti	Atomic ratio		
						H/C/P[a)]	Cl/Ti	P/Ti
1.00	3.82	57.58	7.80	17.66	7.09	14.2/18/0.946	3.37/1	1.70/1
8.93	4.24	58.59	7.83	16.38	6.66	15.5/18/0.933	3.32/1	1.82/1
3.00[b)]	3.98	55.89	7.93	16.53	7.47	15.3/18/0.990	2.99/1	1.64/1

a) The calculated ratio is 15/18/1 for $OPPh_3$. b) An oxidized $TiCl_3$ solution was used as the catalyst.

elemental analysis of the complex are shown in Table 2. The composition depended a little upon the reaction conditions. However, the H/C/P and Cl/Ti ratios were nearly equal to 15/18/1 and 3/1. This shows that a PPh_3 moiety is the sole organic component, and that anionic ligands other than a chloride anion must be present, with a negative charge per titanium ion, since the titanium ion is tetravalent. Thus, the complex must have the following structural features: (1) The titanium ion is tetravalent, (2) a discrete TiO group is present, and (3) the other ligands are chloride anions and $OPPh_3$. Oxotitanium(IV) complexes are apt to have polymeric chain-type structures, *i.e.*, –Ti–O–Ti–O–; complexes such as this complex with discrete titanyl groups (TiO^{2+}) are rare.

There have been no reports on the isolation of the complex formed between $TiCl_3$ and PPh_3. The two d-d transition bands of $TiCl_3$ in acetonitrile under nitrogen, however, were changed a little by the addition of PPh_3; that is, the two bands which were at 585 nm (ε, 25.6) and 680 nm (ε, 15.4) for a triphenylphosphine-free acetonitrile solution of $TiCl_3$ (0.025 M) appeared at 588 nm (ε, 24.3) and 680 nm (ε, 17.7), and at 590 nm (ε, 24.7) and 680 nm (ε, 19.0), when the concentrations of added PPh_3 were 0.104 and 0.203 M respectively. This indicates the presence of a weak interaction between $TiCl_3$ and PPh_3 in an acetonitrile solution.

The oxidation mechanism of $TiCl_3$ with oxygen in acetonitrile seems to be similar to that in pyridine,[3)] involving $Cl_3Ti{-}O_2$ (**2**), $Cl_3Ti{-}O_2{-}TiCl_3$ (**3**), and $Cl_3{-}Ti{-}O$ (**4**) as intermediates. Species like **2**,[5b,10,11)] **3**,[1)] and **4**[10)] have been reported.

The oxidation of PPh_3 catalyzed by **1** had a much slower rate than that catalyzed by $TiCl_3$ (Table 1). Therefore, **1** is not contained in the main catalytic cycle of the $TiCl_3$-catalyzed oxidation, but seems to play a large part in the slow oxygen uptake in the later stage of the oxidation. The **2**, **3**, and/or **4** species reacting with PPh_3 would yield $OPPh_3$ and $TiCl_3$, and also $TiCl_3$ coordinated by PPh_3 would react with oxygen to give **2** coordinated by PPh_3, which would then decompose to $TiCl_3$ and $OPPh_3$. Thus, the main catalytic cycle seems to be composed. Since the oxidation of $TiCl_3$ to **1** was very rapid, the reactions of **2**, **3**, and/or **4** with PPh_3 and the decomposition must also be very rapid.

The authors are grateful to Dr. Toshimitsu Suzuki of this department for his gift of $TiCl_3$.

References

1) D. P. Bauer and R. S. Macomber, *Inorg. Chem.*, **15**, 1985 (1976).

2) S. A. Giddings, *Inorg. Chem.*, **3**, 684 (1964); H. Noeth and R. H. Hartwimmer, *Chem. Ber.*, **93**, 2246 (1960); R. Coutts and R. C. Wailes, *Inorg. Nucl. Chem. Lett.*, **3**, 1 (1967).

3) C. D. Schmulbach, C. C. Hinckley, C. Kolich, T. A. Ballintine, and P. J. Nassiff, *Inorg. Chem.*, **13**, 2026 (1974).

4) IR 1087 cm^{-1} (TiO) for $TiO(acac)_2$: M, Cox. J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, **1965**, 2840.

5) a) Y. Chimura, H. Kanai, S. Yoshida, and K. Tarama, *Chem. Lett.*, **1973**, 1217; b) Y. Chimura, *ibid.*, **1974**, 393; c) Y. Chimura, M. Beppu, S. Yoshida, and K. Tarama, *ibid.*, **1976**, 375.

6) R. J. H. Clark, J. Lewis, D. J. Machin, and R. S. Nyholm, *J. Chem. Soc.*, **1963**, 379.

7) This complex was prepared by the partial hydrolysis of $TiCl_4(CH_3CN)_2$: A. Feltz, *Z. Anorg. Allg. Chem.*, **332**, 35 (1964).

8) G. B. Deacon and J. H. S. Green, *Chem. Ind. (London)*, **1965**, 1031.

9) IR 975 cm^{-1} (TiO) for $[N(C_2H_5)_4]_2[TiOCl_4]$: A. Feltz, *Z. Anorg. Allg. Chem.*, **334**, 242 (1965).

10) J. H. Lunsford, *Catal. Rev.*, **8**, 135 (1973).

11) B. R. McGarvey and E. L. Tepper, *Inorg. Chem.*, **8**, 498 (1969).