PHOTOCHEMICAL REACTIONS OF BIS(η^5-CYCLOPENTADIENYL)-TITANIUM DICHLORIDE

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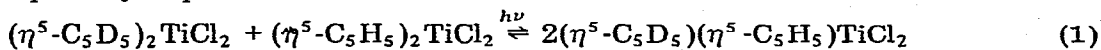
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Summary

Irradiation of benzene solutions 10^{-3} M in both titanocene-d_{10} dichloride and titanocene dichloride with light of wavelengths 313, 360, 400, and 520 nm leads to the formation of titanocene-d_5 dichloride with quantum yields of 0.02, 0.005, 0.01 and 0.007 mol Ei^{-1}, respectively. Photodecomposition of titanocene dichloride is negligible even at much longer photolysis times than those required for isotopic equilibration. Photolysis of benzene solutions 10^{-2} M in titanocene dichloride and 1.0 M in methanol leads to the formation of cyclopentadienyl-(methoxo)titanium dichloride with a quantum yield of about 0.08 mol Ei^{-1} when the irradiating wavelength is 313 nm.

Introduction

The photochemistry of titanocene derivatives has recently attracted attention [1—3] commensurate with the importance of those compounds in current organometallic chemistry. In this paper the exchange of η^5-cyclopentadienyl ligands between identical transition metal complexes, as represented in particular by eq. 1 is examined in more detail. We also expand the report on methanolysis of titanocene dichloride according to eq. 2 which proceeds exclusively by a photolytic process.

$$(\eta^5\text{-}C_5D_5)_2TiCl_2 + (\eta^5\text{-}C_5H_5)_2TiCl_2 \overset{h\nu}{\rightleftharpoons} 2(\eta^5\text{-}C_5D_5)(\eta^5\text{-}C_5H_5)TiCl_2 \qquad (1)$$

$$(\eta^5\text{-}C_5H_5)_2TiCl_2 + MeOH \rightarrow (\eta^5\text{-}C_5H_5)(OMe)TiCl_2 + C_5H_6 \qquad (2)$$

Experimental

Titanocene dichloride obtained from Alfa Products was recrystallized in a Soxhlet apparatus from chloroform saturated with HCl, under HCl and argon, and was then sublimed. Perdeuterotitanocene dichloride was prepared by the

procedure of Brintzinger and Marvich [4], wherein $[Cp_2TiH]_x$ was stirred in toluene under deuterium gas for at least 30 h, then cooled to $-70°C$ and treated with HCl gas. The product was purified as above. Isotopically pure $(C_5D_5)_2TiCl_2$, with a parent ion isotopic peak distribution identical to that of the undeuterated species, was obtained if pure deuterium gas was added several times during the deuteration.

Photolyses were effected by use of a 450 W medium pressure mercury lamp, Hanovia #679A0360, which was mounted in a quartz cooling jacket through which tap water circulated. This assembly was mounted concentrically inside a 70 mm quartz filter solution cell, providing a 1.0 cm filter path. When a second filter solution was required, a 120 mm pyrex cell, providing a 1.9 cm path, was mounted concentrically outside the apparatus described above. The lamp and filter cells were mounted inside a merry-go-round sample rotator [5] to assure the uniform illumination of all samples and actinometer solutions. Temperature fluctuations were moderated by immersing the entire apparatus in an alcohol/water bath.

Potassium Reineckate [6] and/or Valerophenone [7] actinometers having the same optical absorbance as the sample at the irradiating wavelength, were photolyzed exactly as the samples were.

Filter solutions were as follows: 313 nm: $0.0020\ M\ K_2CrO_4$ in $0.07\ M$ K_2CO_3 (1 cm) + $0.96\ M\ CoSO_4$ (1.9 cm); 365 nm: Corning #7-83 combination glass filter; 400 nm: $0.42\ M\ CuSO_4$ in $3.3\ M\ NH_4OH$ (1 cm); 520 nm: $1.5\ M$ $CuCl_2$ in $2.4\ M\ CaCl_2$ (acidified, 1.0 cm) + $0.16\ M\ CuSO_4$ in NH_4OH (optional, for low intensity study).

Sample solutions were prepared by dissolving a weighed quantity of the solid in benzene in an argon atmosphere glove box. The solution (3.0 ml aliquots) was added to 13 X 100 mm pyrex culture tubes with a syringe. The tubes were securely stopped and sealed with an oxypropane torch. After measured periods of photolysis (typically 1 to 2 h), several sample cells were removed, pooled, and the photolyte was evaporated to dryness and sublimed before the mass spectrum was obtained by use of a Perkin—Elmer RMU-6 mass spectrometer. The optical absorbance at 520 nm was routinely checked several times during each run to determine the extent of photodecomposition. The absence of

TABLE 1

MASS SPECTROGRAPHIC DATA FOR THE PERDEUTEROTITANOCENE DICHLORIDE/TITANOCENE DICHLORIDE LIGAND EXCHANGE

t (h)	Normalized intensities (m/e)										I_{253}/I_{258}	F
	248	253	258	65	66	67	68	69	70	71	72		
0.0	71	4	100	100	37	9	6	17	71	21	4	0.04	0.025
2.5	71	48	100	100	39	8	5	17	73	22	4	0.48	0.30
5.0	67	84	100	100	34	7	6	17	73	18	4	0.84	0.52
7.5	68	115	100	100	34	6	5	17	72	17	5	1.15	0.72
10.0	69	135	100	100	39	7	5	7	70	21	4	1.35	0.84
12.5	67	145	100	100	41	8	6	_J	71	22	5	1.45	0.91
15.0	67	151	106	100	37	8	5	17	72	20	4	1.51	0.94
17.5	65	155	100	100	49	9	6	20	68	30	5	1.55	0.97
52	67	163	100	100	38	6	4	17	75	15	4	1.63	1.0

thermal exchange was demonstrated by allowing a sample (benzene solution) to reflux for 72 h in the dark, and obtaining the mass spectrum of the titanocene dichloride species. No peak corresponding to the d_5 species appeared in the mass spectrum.

For photomethanolysis experiments, samples were prepared as above and methanol was added by syringe to give the desired concentration. The samples were withdrawn at approximately 10 min photolysis periods, and the absorbance at 520 nm was measured by a Unicam model SP 800 recording spectrophotometer with matched, 1 cm quartz cells. The decrease in A_{520} was taken as the index to the extent of photomethanolysis. The product could be recrystallized from the photolyte solution, and had a melting point of $100°C$. The mass spectrum of the product had prominant peaks at $m/e = 214$ $[(\eta^5\text{-}C_5H_5)Ti(OCH_3)Cl_2^+]$; 179 $[(\eta^5\text{-}C_5H_5)Ti(OCH_3)Cl^+]$; 149 $[Ti(OCH_3)Cl_2^+]$; and 148 $[(\eta^5\text{-}C_5H_5)TiCl^+]$.

Results

Table 1 shows the pertinent peaks in the mass spectrum of samples irradiated for varying times with light of 313 nm wavelength and intensity of 0.006 Ei l^{-1} h^{-1}. The peak at $m/e = 253$, corresponding to titanocene-d_5 dichloride, increases relative to the peaks at $m/e = 248$ and 258, corresponding to the d_0 and d_{10} species, respectively, as photolysis time increases. These peaks appear in manifolds which arise due to the presence of ^{37}Cl, ^{35}Cl, ^{46}Ti, ^{47}Ti, ^{49}Ti, ^{50}Ti, ^{12}C and ^{13}C isotopes. These manifolds would obscure the contribution of ring hydrogen exchange if it occurred, so the intensities of the peaks between $m/e = 65$ and 72 are reported (normalized separately) to demonstrate that this process does not occur.

The ratio of the intensities of the $m/e = 253$ and 248 peaks, I_{253}/I_{248}, computed for each irradiation time, and divided by its equilibrium value, gives the fraction of exchange, F, complete in that time period. The equilibrium value was determined by irradiating samples for up to 86 h, a period 10 times that required to reach a constant ratio. Although the optical absorbance at 520 nm decreased by a maximum of 6% in the first 24 h of photolysis, it remained constant after that, suggesting that the only side reaction is with small amounts of impurities. $\ln(1 - F)$ against photolysis time was plotted for each sample [8].

TABLE 2

DATA FOR THE CYCLOPENTADIENIDE EXCHANGE PROCESS

λ (nm)	Intensity	Sample concentrations ($M \times 10^3$)		$-$Slope $\pm \sigma$ $\ln(1 - F)$ vs. t	ϕ
		[Cp$_2$TiCl$_2$]	[Cp$_2$-d_{10}-TiCl$_2$]		
520	0.07	2.1	1.7	0.0173 $\pm$ 0.012	0.007
520	0.003	2.1	1.7	0.027 [a]	0.01
400	0.03	2.6	2.2	0.039 $\pm$ 0.008	0.01
365	0.006	2.1	1.7	0.034 $\pm$ 0.002	0.005
313	0.009	2.2	1.6	0.294 $\pm$ 0.028	0.02
		1.0	0.8	0.538 $\pm$ 0.032	0.02

[a] Only three points were determined, hence no statistics are given.

The most probable slope of the line was calculated by a standard least squares treatment of the data [19], and the rate was calculated by using [9] the eq. 3, where [A] and [B] represent concentrations of the exchanging species.

$$\text{slope} = -R \left[\frac{[A] + [B]}{[A] \times [B]} \right] \tag{3}$$

Quantum yields were calculated by dividing the rate (in $M\ h^{-1}$) by the intensity of the absorbed light (in $Ei\ l^{-1}\ h^{-1}$). The light intensity was constant, as required by this procedure, and ranged from about 0.1 to about 0.003 $Ei\ l^{-1}\ h^{-1}$ depending on the experiment.

Table 2 summarizes the data obtained for the exchange process. The quantum yields calculated from the intensity measured with the valerophenone actinometer at 313 nm was about 3 times as great as those calculated from the intensity measured by the potassium Reineckate actinometer (shown in Table 2). This discrepancy apparently arises because the Reineckate absorbs above 600 nm, a region which was not eliminated by the filter system. The samples do not absorb at 600 nm.

The equilibrium constant for the exchange reaction 1, calculated from the intensities of the m/e = 253, 258, and 248 peaks by using the equation: $K = I_{253}^2 /(I_{248} \times I_{258})$, has the predicted value of 4.0. The present system is analogous to the D_2O/H_2O system with respect to the predicted entropy change [9], and since the enthalpy change is essentially zero, the free energy and equilibrium constant can be calculated easily.

The photomethanolysis proceeded with a quantum yield of about 0.08 mol Ei^{-1} when the Cp_2TiCl_2 concentration was 8.1×10^{-3} and the methanol concentration was 1.0 M, and a quantum yield of about 0.05 when the Cp_2TiCl_2 concentration was 4.05×10^{-3} and methanol concentration was 0.25 M. The absorbance at 520 nm was stable for samples stored in the dark for 36 h for both photolyzed and unphotolyzed samples, indicating that there are no secondary thermal processes.

Discussion

The photolability of the η^5-cyclopentadienyl ligand on titanocene dichloride is surprising in view of its thermal stability in most chemical environments. For instance, titanocene dichloride is not subject to thermal alcoholysis and other substitution reactions that occur readily in bis(alkoxo)titanocene derivatives [10,11]. Titanocene dichloride will not yield ferrocene by reaction with ferrous chloride [10] or nickelocene by reaction with nickel carbonyl [12]. Notable thermal reactions involving the η^5-cyclopentadienyl ligand on titanocene dichloride are amine cleavage [13] and redistribution reactions with $TiCl_4$ [14].

Since the cyclopentadienide exchange reaction is not accompanied by decomposition, we hesitate to propose a mechanism in which cyclopentadiene free radicals are produced following a photoinduced charge transfer to the titanium center. Harrigan, et al. [1] have proposed such a mechanism for the photochemical substitution of cyclopentadienide by Cl, but we have been unable to observe, as they did, evidence for the formation of any new products from titanocene dichloride in benzene, under any photolysis conditions. The small

decrease in titanocene dichloride concentration (as indicated by a decrease in A_{520}) that we observed in the initial period of photolysis and attribute to impurities may explain the discrepant observations.

The visible spectrum of titanocene dichloride has three bands which can be interpreted in terms of the MO diagram [15,16] as charge transfer transitions. Two of these transitions terminate in non-bonding a_1 (d_z2) and b_1 (d_{xy}) titanium orbitals, and one in an antibonding a_1 $(d_{x^2-y^2})$ orbital. More vibrational excitation would accompany the latter, and it is reasonable to assign it to the broad, short wavelength (λ_{max} = 280 nm) band. It is also reasonable that the highest quantum yields were observed for photolysis involving the latter transition, since the most bond destabilization would occur. But, because irradiation in all absorption bands leads to reaction suggests to us that reduction hapticity may be as reasonable a proposal as bond cleavage and free radical formation for the initial step in the mechanism. The rapid thermal halide exchange between Cp_2TiCl_2 and Cp_2TiBr_2 [3] demonstrates that there is a thermal coordination sphere reduction mechanism which might be a prerequisite for the photochemical reaction.

Previous attempts [10] to prepare η^5-cyclopentadienyl(alkoxo)titanium dichlorides by refluxing titanocene dichloride in alcohol were successful, we presume, only to the extent that photolytic pathways contributed. The photolytic methanolysis of titanocene dichloride shown in eq. 2 yields a product that was previously obtainable only through more difficult pathways, including the treatment of cyclopentadienyltitanium trichloride with methanol [17]. Photomethanolysis does not lead to the products obtained by the thermal addition of alcohols to cyclopentadienyltitanium dichloride [18], and this may suggest that $CpTiCl_2$ is not an important intermediate in the photolyses. High methanol concentrations in the photolysis samples, or long irradiation times, produced darker products (or product mixtures) so the reaction apparently becomes complex under such conditions.

Acknowledgement

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