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Kinetic Studies of the Hydrolysis of (h^5-Methylcyclopentadienyl)(h^5-Cyclopentadienyl)titanium Dichloride

D. PACHECO,[a] M. I. HERNANDEZ,[a] J. J. LUBINKOWSKI* and J. L. CALDERÓN[a]

Centro de Petróleo y Química, Instituto Venezolano de Investigaciones Científicas (IVIC), Apartado 1827, Caracas, Venezuela[a]

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The synthesis of polyesters from the condensation reactions of various diacid salts with metallocene dichlorides via the interfacial technique has been recently reported.[1-3] In addition to the previously demonstrated formation of $(C_5H_5)_2Ti(OH)^+$ in aqueous solution,[4] we have found that polymers formed via the interfacial technique have hydroxyl groups incorporated in the polyester chains. The latter could possibly be the products of competitive hydrolysis reactions. As a result, we carried out kinetic studies with the use of stopped-flow techniques. These studies clearly demonstrate that hydrolysis has a significant role and would compete with the formation of the polymer of the desired repetitive unit.

We investigated the formation of $RR'Ti(OH)^+$ (where R = h^5-C_5H_5 and R' = h^5-$C_5H_4CH_3$) as follows: in each experiment a solution of $RR'TiCl_2$[5] in dry dioxane was reacted with an aqueous dioxane solution or with an aqueous solution of sodium hydroxide in dioxane. The reactions were carried out at 25.0 ± 0.1 °C in a Durrum stopped-flow with a Kel-F reaction cell of 20 mm path length immersed in a water reservoir. A Pye Unicam 1800 spectrophotometer was used for spectral characterization of the species, and these results were compared with those previously reported.[6] Digitalizations of the analog output of the stopped-flow were carried out manually from Polaroid films taken from the oscilloscope traces. A Fortran program was used for the curve fitting of the following reaction scheme,

Scheme I

$$RR'TiCl_2 \xrightarrow{k_{12}} RR'TiCl^+ + Cl^- \quad \text{(I-a)}$$

$$RR'TiCl^+ \xrightarrow{k_{23}} RR'Ti^{+2} + Cl^- \quad \text{(I-b)}$$

$$RR'Ti^{+2} + OH^- \xrightarrow{k_{34}} RR'Ti(OH)^+ \quad \text{(I-c)}$$

and according to the empirical rate-law shown in Scheme II:

Scheme II

$$\frac{d[RR'TiCl_2]}{dt} = -k_{12}[RR'TiCl_2] \quad \text{(II-a)}$$

$$\frac{d[RR'TiCl^+]}{dt} = -k_{12}[RR'TiCl_2] - k_{23}[RR'TiCl^+] \quad \text{(II-b)}$$

$$\frac{d[RR'Ti^{+2}]}{dt} = k_{23}[RR'TiCl] - k_{34}[RR'Ti^{+2}][OH^-]^n \quad \text{(II-c)}$$

$$\frac{d[RR'Ti(OH)^+]}{dt} = k_{34}[RR'Ti^{+2}][OH^-]^n \quad \text{(II-d)}$$

which is a first-order approximation of the system shown below in Scheme III,

Scheme III

$$RR'TiCl_2 \rightleftharpoons RR'TiCl^+ + Cl^- \qquad k_{12}, k_{21}, K_1 \quad \text{(III-a)}$$

$$RR'TiCl^+ \rightleftharpoons RR'Ti^{+2} + Cl^- \qquad k_{23}, k_{32}, K_2 \quad \text{(III-b)}$$

$$RR'Ti^{+2} + OH^- \rightleftharpoons RR'Ti(OH)^+ \qquad k_{34}, k_{43}, K_3 \quad \text{(III-c)}$$

The correlation factor of the experimental data with respect to the first-order approximation is greater than 0.985. In addition, the estimations of K_1, K_2 and K_3 were carried out by means of computer simulation of the analog output of the stopped-flow from extrapolation to the infinite time of the reaction with a correlation factor of 0.981 ± 0.002 in the particular case of $XH_2O = 2.8 \times 10^{-1}$.

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*Visiting Professor from Departamento de Química, Universidad Simón Bolívar, Apartado 5354, Caracas, Venezuela.

Such correlations were possible in light of experimental evidence which demonstrated that the dissociation of $RR'TiCl_2$, in pure dioxane, was negligible within the limits of experimental error.

The results which are shown in Tables I and II indicate that the formation of the monocation $RR'TiCl^+$ is a first-order process dependent solely on the concentration of the organo-titanium compound $RR'TiCl_2$. Likewise the conversion of $RR'TiCl^+$ to the dication $RR'Ti^{+2}$ is also a first-order process. Furthermore, our initial studies indicate that the formation of the monohydroxy species $RR'Ti(OH)^+$ depends on the concentration of both the titanium species $RR'Ti^{+2}$ and the hydroxide ion. The relatively fast ionization of the organotitanium compound $RR'TiCl_2$, as demonstrated by the k values indicated in Tables I and II, reinforces the suggestion of the formation of the ionic intermediate species.[7] However, the formation of the monohydroxy species, dependent on the constant k_{34}, under the above conditions must therefore compete significantly with the polymerization process.

TABLE I. Dependence of k_{12} and k_{23} on the Mol Fraction of Water.[a]

xH_2O[b] × 10	k_{12}[c] (sec^{-1})	No. of Runs	k_{23}[d] (sec^{-1})	No. of Runs
0.45	1.9 ± 0.1	3	0.2	2
0.12	1.5 ± 0.2	2	0.3	2
0.17	1.6 ± 0.2	4	0.3	2
0.21	1.8 ± 0.2	3	0.2	1
0.25	1.7 ± 0.1	3	0.3	3
0.28	1.7 ± 0.2	8	0.3	6

[a] At (25.0 ± 0.1) °C and $[RR'TiCl_2] = 5.0 \times 10^{-4}$. [b] Mol fraction. [c] Errors are standard deviations. [d] The general standard deviation of k_{23} is 0.08.

TABLE II. Dependence of k_{12} and k_{23} on $RR'TiCl_2$.[a]

$[RR'TiCl_2]$ × 10^4 (*M*)	xH_2O[b] × 10	k_{12}[c] (sec^{-1})	No. of Runs	k_{23}[d] (sec^{-1})	No. of Runs
1.26	0.27	1.5 ± 0.2	3	0.3	3
5.02	0.27	1.9 ± 0.2	3	0.3	2
2.50	0.27	2.0 ± 0.1	3	0.2	3
1.00	0.27	1.7 ± 0.2	3	–	–
0.51	0.27	2.0 ± 0.2	3	0.3	3

[a] 25.0 ± 0.1 °C. [b] Mol fraction. [c] Errors are standard deviations. [d] The general standard deviation of k_{23} is 0.09.

In solving the empirical rate law (Scheme II), we have made the assumption that at $t = 0$, $[RR'Ti^{+2}] = 0$; therefore, for the first and second half-lives of the reaction $[RR'Ti^{+2}] \ll [OH^-]$ and equations (II-c) and (II-d) would be:

$$\frac{d[RR'Ti^{+2}]}{dt} = k_{23}[RR'TiCl^+] - k_{obs}[RR'Ti^{+2}] \tag{II-c'}$$

$$\frac{d[RR'Ti(OH)^+]}{dt} = k_{obs}[RR'Ti^{+2}] \tag{II-d'}$$

where $k_{obs} = k_{34}[OH^-]^n$; this assumption, although arbitrary, allows one for the curve fitting of the function:

$$[RR'Ti^{+2}] = \Phi[\exp(-k_{12}t) - \exp(-k_{23}t) - \exp(-k_{34}t)]$$

$$\text{where } \Phi = \frac{k_{12}k_{23}[RR'TiCl_2]}{(k_{23} - k_{12})(k_{obs} - k_{12})}$$

The dependence of the k_{obs} upon the hydroxide ion concentration shown in Table III indicates conclusively that the formation of the cation $RR'Ti(OH)^+$ can compete effectively with the polymerization process occurring in the interfacial method. Since the time domain of reaction 34 (100 to 200 seconds) is considerably shorter than the time domain of the polymerization reaction which we have observed, the formation of the cation $RR'Ti(OH)^+$ would

TABLE III. Dependence of k_{obs} on $[OH^-]$.[a]

xH_2O × 10[b]	$[OH^-]$ × 10^{-4} (*M*)	$RR'TiCl_2$ × 10^4 (*M*)	k_{obs} × 10^{-2} [c,d] (sec^{-1})
0.26	0.02	5.04	2.9 ± 0.3
0.26	2.44	5.04	3.2 ± 0.2
0.26	3.65	5.04	3.4 ± 0.2
0.26	4.88	5.04	4.5 ± 0.1
0.26	6.10	5.04	7.7 ± 0.1
0.26	7.32	5.04	17.3 ± 0.5

[a] At (25.0 ± 0.1) °C. [b] Mol fraction. [c] Errors are standard deviations. [d] After uncalibration of the time scale of the oscilloscope, k_{obs} was measured with the use of stopped flow by following manually the time monitoring of at least three different runs for each experiment.

TABLE IV. Approximate Values of K_1, K_2, K_3.[a,b]

xH_2O × 10	$K_1 \times 10^{-5}$	$K_2 \times 10^{-5}$	$K_3 \times 10^{-6}$
0.45	2.0	4.0	7.0
0.25	1.0	2.0	4.0
0.17	1.0	2.0	3.0

[a] At (25.0 ± 0.1) °C. [b] The average standard deviation of K_1, K_2 and K_3 is 0.3.

effectively compete with the polymerization process occurring in the interfacial method. In addition, the values of K_1, K_2 and K_3 from Table IV demonstrate that the stability of the monohydroxylated species $RR'Ti(OH)^+$ is of sufficient magnitude as to disfavor the reverse reaction leading to the formation of the dication species $RR'Ti^{+2}$.

Studies are now being conducted in order to further clarify the mechanistic considerations in this communication.

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