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NOTE

ELECTROCHEMICAL INVESTIGATION OF σ-BONDS IN π-COMPLEXES OF SOME TRANSITION METALS

VI. POLAROGRAPHIC REDUCTION OF DICYCLOPENTADIENYLTITANIUM COMPLEXES CONTAINING LOCALIZED σ-BONDS Ti–C

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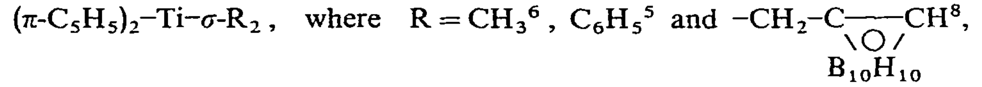
Electrochemical reduction of the transition metal–carbon σ-bonds in the 18-electron metal carbonyl complexes: π-$C_5H_5Fe(CO)_2$–σ-R[1], π-$C_5H_5W(CO)_3$–σ-R[2] and $(CO)_5M$–σ-R (M = Mn and Re)[3] was discussed in detail in the previous papers of this series. In all these cases two electrons have been shown to transfer to the antibonding orbital of the metal–carbon σ-bond, leading to its homolytic cleavage. The thermodynamic stability of the carbanion generated was found to be rate-determining. In passing from one complex to another with R unvarying, the reaction rate changed negligibly. Electron and coordinate saturation makes their reduction practically insensitive to variations in medium and supporting electrolyte.

In the present work, some dicyclopentadienyltitanium σ-derivatives, $(\pi\text{-}C_5H_5)_2$-Ti-$(\sigma\text{-}R)_2$, were investigated within the same terms. Such derivatives are neither electronically nor coordinatively saturated.

In our previous study[4], reduction of the respective halides was found to be similar to that of the mercury derivatives rather than of transition metal halides. In the present work we have studied the polarographic reduction of the following titanium derivatives:



$$(\pi\text{-}C_5H_5)_2\text{–}Ti\text{–}\sigma\text{-}R_2, \quad \text{where} \quad R = CH_3{}^{6},\ C_6H_5{}^{5} \text{ and } -CH_2-\underset{B_{10}H_{10}}{\underset{\backslash O /}{C\text{——}CH^{8}}},$$

on the dropping mercury electrode (DME) in aprotic medium.

All the complexes investigated were prepared by procedures described and had characteristics in accordance with those published[5–8]. The experimental procedure was reported in our previous paper[1].

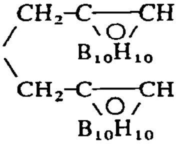
RESULTS AND DISCUSSION

The data on the polarographic reduction of the compounds investigated are listed in Table 1.

Compounds I and II in DMF (Fig. 1) give one well-defined diffusion reduction wave: its limiting current is proportional to concentration and $\sqrt{H}$; the temperature

TABLE 1

POLAROGRAPHIC CHARACTERISTICS OF $(\pi\text{-}C_5H_5)_2\text{-}Ti{<}^{R}_{R}$ IN 0.1 N $(C_2H_5)_4NClO_4$, DMF, SCE, $c=2\cdot10^{-3}$ M, $t=0.37$ sec

No.	$^{\diagup R}_{\diagdown R}$	$-E_{\frac{1}{2}}$ (V)	i_d (μA)	n
I	$\diagup C_6H_5$ $\diagdown C_6H_5$	1.46	1.22	1
II	$\diagup CH_3$ $\diagdown CH_3$	1.91	1.35	1
III	$\diagup CH_3$	0.14[a]	0.6	
	$\diagdown Cl$	1.17[b]	0.2	
IV	$\diagup Cl$	0.18[a]	0.4	
	$\diagdown Cl$	0.63	1.0	(2) 1
		1.94	1.6	(3) 1
V	 $\diagup CH_2\text{-}\underset{\diagdown O \diagup B_{10}H_{10}}{C\text{——}CH}$ $\diagdown CH_2\text{-}\underset{\diagdown O \diagup B_{10}H_{10}}{C\text{——}CH}$	0.96	1.3	
		2.13	2.0	

[a] anodic wave; [b] wave is poorly defined.

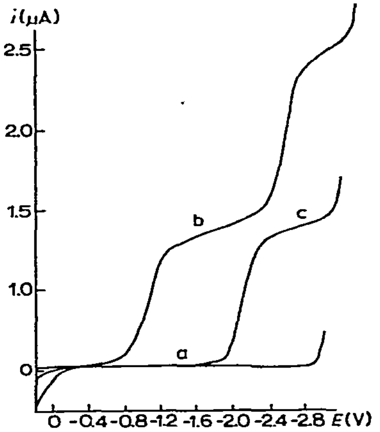
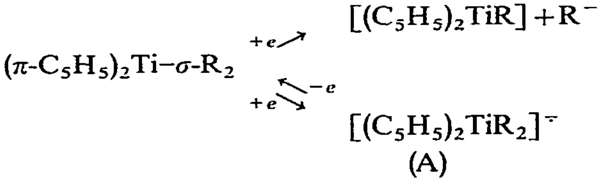


Fig. 1. Polarograms of $(C_5H_5)_2TiR_2$ ($R=CH_3$, $CH_2\text{-}\underset{\diagdown O\diagup B_{10}H_{10}}{C\text{——}CH}$) in 0.1 N $(C_2H_5)_4NClO_4$, DMF, SCE, $c=2\cdot10^{-3}$ M. (a) curve of supporting electrolyte; (b) polarogram of $(C_5H_5)_2Ti(CH_2\text{-}\underset{\diagdown O\diagup B_{10}H_{10}}{C\text{——}CH})_2$; (c) polarogram of $(C_5H_5)_2Ti(CH_3)_2$.

coefficient is 1%. Microcoulometric measurements show that the number of electrons corresponds to a one-electron process ($n=0.68$). Reduction potentials for I and II are dependent on concentration: a ten-fold increase in concentration shifts $E_{\frac{1}{2}}$ by 50 mV to negative values and the slope of $\log[i/(i_d-i)]/E$ is 100 mV. Measurements with a Kalousek commutator method indicate that reduction is an irreversible process. On replacing DMF by CH_3CN in the reduction of I and II at the unchanging cathodic wave*, we observed a well-defined diffusive irreversible wave in the anodic area ($E_{\frac{1}{2}} = +0.20$ V). No detailed investigation of this oxidation wave was carried out in this work.

Electron addition may involve two mechanisms:



$$(\pi\text{-}C_5H_5)_2Ti\text{-}\sigma\text{-}R_2 \begin{cases} \xrightarrow{+e} [(C_5H_5)_2TiR] + R^- & (1) \\ \underset{-e}{\overset{+e}{\rightleftarrows}} \underset{(A)}{[(C_5H_5)_2TiR_2]^{\overline{\cdot}}} & (2) \end{cases}$$

Mechanism (2) is least probable since the reduction was found to be irreversible. Furthermore, after chemical reduction of (I) with sodium amalgam, the resulting solution gave no anodic waves within the region, 0 to −2.8 V, which indicated that no oxidation of the obtained anion-radicals took place.

We may thus assume that under the conditions of our experiment, reduction of $(\pi\text{-}C_5H_5)_2Ti\text{-}\sigma\text{-}R_2$ is a one-electron process involving a cleavage of the Ti–R σ-bond.

At the potentials investigated, the primary reduction product is inactive polarographically at the first stage**. It probably further reduces at more negative potentials that are beyond the discharge range of the supporting electrolyte.

Compound III in DMF gives two waves***: an anodic wave with $E_{\frac{1}{2}}$ almost equal to that of IV, and a poorly-defined cathodic wave. As in the case of the dichloride, the cathodic wave is observed preferably in 0.1 *N* LiCl ($E_{\frac{1}{2}} = -1.17$ V). A comparison of $E_{\frac{1}{2}}$ values for III with the first cathodic wave of IV ($E_{\frac{1}{2}} = -0.63$ V) shows that one methyl group instead of chlorine inhibits the first reduction stage. It is thus clear, that introduction of two methyls in II should inhibit its reduction even further. Such a reaction scheme is in a good agreement with the results of the reduction of V having two carboranyl groups. The known strong electron-attracting effect of the carboranyl group[10] causes the potential to shift by almost 1 V to its positive value in the reduction of the dimethyl derivative of II. The same effect shifts the potential of the second reduction stage; thus the well-defined diffusion wave becomes observable in the measurable potential area.

That is, in the general case, compounds with the Ti–C σ-bond reduce as in the following scheme:

$$(C_5H_5)_2TiR_2 + e \rightarrow [(C_5H_5)TiR] + R^- \qquad (3)$$

$$(C_5H_5)_2TiR + e \rightarrow [(C_5H_5)_2Ti] + R^- \qquad (4)$$

As in the case of the dihalides, the primary product of the second reduction stage of compound IV is dicyclopentadienyl titanium. The possibility of the chemical reduction of II to titanocene has already been described[6].

The potential difference for the first and second reduction stages of V is equal

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* Owing to the higher viscosity of the solution, the limiting current increased in CH_3CN[9], as would be expected.

** At the potential of the limiting current of the reduction wave (−2.4 V) a signal from the tervalent titanium was registered in a cell of the resonator of an ESR spectrometer.

*** We observed another poorly defined cathodic wave at more negative potentials (−1.8 V).

to 1.2 V, *i.e.*, about the same as for the dichloride IV. On the other hand, for analogous mercury derivatives such a difference is so small that the reduction involves only a two-electron stage.

The facility of reduction of the Ti–C σ-bond in relation to R is the same (carboranyl > phenyl > methyl) as in the case of the other σ-compounds investigated, either transition or non-transition metals. Also, potential differences between two derivatives of titanium ($\Delta E_{\frac{1}{2}}$ (CH_3–C_6H_5) = 0.45 V) and mercury ($\Delta E_{\frac{1}{2}}$ = 0.4 V)[11] are almost the same.

It may thus be assumed that the thermodynamic stability of the carbanion generated again determines the rate of the σ-bond cleavage in a one-electron process.

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