The authors wish to express their gratitude to L. B. Volodarskii, in whose laboratory the other oximes have been synthesized, used in the present work; to V. I. Savin for supplying a sample of N,N'-dibenzylhydrazine and for assisting in the GC analysis; and to N. G. Gazetdinova for performing the TLC analyses of the solutions after electrolysis.

## CONCLUSIONS

1. The electrochemical reduction of some oximes and  $\alpha$ -hydroxylaminooximes in a nonaqueous medium represents an irreversible four-electron process, involving kinetic limitations.

2. Difference between the electrochemical behavior of geometrical isomers of the oximes in a nonaqueous medium have been demonstrated.

## LITERATURE CITED

- 1. T. V. Troepol'skaya, E. N. Munin, and Yu. P. Kitaev, Izv. Akad. Nauk SSSR, Ser. Khim., 982 (1979).
- 2. H. Lund, Acta Chem. Scand., 13, 249 (1959).
- 3. M. S. Sethi, P. S. Raghavan, R. P. Singh, K. Mahendra, and B. S. Gard, Microchem. J., 25, 129 (1980).
- 4. N. A. Akmanova, Kh. F. Sigitdinova, and L. A. Kulikovskaya, Zh. Obshch. Khim., 48, 2737 (1978).
- 5. M. V. Damel, P. Tivari, P. T. Malshe, and R. Kaushal, Bull Soc. Chim. Belg., 89, 1015 (1980).
- 6. N. Tyutyulkov, Zh. Fiz. Khim., 32, 1389 (1958).
- 7. T. V. Troepol'skaya, G. A. Vagina, V. I. Morozov, and Yu. P. Kitaev, Izv. Akad. Nauk SSSR, Ser. Khim., 512 (1983).
- 8. A. G. Stromberg and T. M. Markacheva, Zh. Fiz. Khim., 28, 671 (1954).
- 9. E. Beckman, Chem. Ber., 23, 1684 (1890).
- E. Beckman, Chem. Ber., 22, 605 (1898).
   R. Huisgen, W. Rapp, I. Udi, H. Walz, and E. Mergenthaler, Liebigs Ann. Chem., 586, 1 (1954).
- 12. L. B. Volodarskii, V. A. Koptyug, and A. N. Lysak, Zh. Obshch. Khim., 2, 114 (1966).
- 13. C. Amatore, J. Pinson, and J. M. Saveant, Electroanalyt. Chem., 107, 75 (1980).
- 14. C. Amatore, J. Pinson, and J. M. Saveant, Electroanalyt. Chem., 107, 75 (1980).
- 15. Lun-Shu R. Yeh and A. J. Bard, Electroanalyt. Chem., 124, 189 (1977).

## POLAROGRAPHY OF SUBSTITUTED AND BRIDGED BIS(CYCLOPENTADIENYL)-

TITANIUM DICHLORIDES IN TETRAHYDROFURAN

- V. V. Strelets, G. L. Soloveichik,
- A. I. Sizov, B. M. Bulichev,
- A. Rusina, and A. A. Vlchek

The electroreduction of  $Cp_2TiCl_2$  (where Cp is  $\eta^5-C_5H_5$ ), which has been studied in several publications [1-4], proceeds stepwise in aprotic medium, and can be represented by the following scheme:

$$Cp_2TiCl_2 \xrightarrow{e} Cp_2TiCl \xrightarrow{e} Cp_2Ti \xrightarrow{e} Cp_2Ti \xrightarrow{e} Cp_2Ti$$

Substituents in the cyclopentadiene ring can have a substantial effect on the half-wave potentials  $(E_{1/2})$  of the individual steps and on the stability of the reduction intermediates, particularly because of electronic and steric effects. The most convenient materials for studying the effects on  $E_{1/2}$  are the substituted bis-cyclopentadienyl dichlorides of Ti, which contain alkyl groups in the ring, or alkylidene bridges that tie two rings together.

Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka Branch; Institute of New Chemical Problems, Academy of Sciences of the USSR, Chernogolovka; Ya. Geirovskii Institute of Physical Chemistry and Electrochemistry, Academy of Sciences of the Czechoslovak SSR, Prague. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2493-2497, November, 1983. Original article submitted January 26, 1983.

0568-5230/83/3211-2241\$07.50 © 1984 Plenum Publishing Corporation

2241

UDC 543.253:541.49:547. 514.721:546.822'131 We have studied the polarographic reduction in tetrahydrofuran (THF) of  $(C_5H_5)_2TiCl_2$  (I),  $(MeC_5H_4)_2TiCl_2$  (II),  $(C_5Me_5)_2TiCl_2$  (III), which are known compounds, and  $(t-BuC_5H_4)_2TiCl_2$  (IV), which we synthesized, and the bridge compounds of the general formula  $(CH_2)_n(C_5H_4)_2$ -TiCl<sub>2</sub>, where n = 1 (V), 2 (VI), and 3 (VII).

#### EXPERIMENTAL

Compounds I-III and V-VII were synthesized by known methods [5-7].

<u>Bis(tert-butylcyclopentadienyl)titanium Dichloride (IV).</u> To a suspension of 2.4 g of metallic Na in 250 ml of THF at ~20°C was added 12 ml of tert-butylcyclopentadiene, obtained according to [8]. After 2 h, a solution of 5.6 ml of n-BuCl in 50 ml of THF was added dropwise and the mixture was stirred for 10 h. Precipitated NaCl and excess Na were filtered off. To the filtrate at 0°C was added a solution of 1.5 ml of TiCl<sub>4</sub> in a mixture of 50 ml of benzene and 30 ml of THF. The mixture was stirred for 3 h at ~20°C and then saturated with dry HCl, and the solvent was evaporated in vacuum. The residue was extracted with HCl-saturated CHCl<sub>3</sub>. There was obtained 5.1 g (90%) of brick-colored crystals which were purified by recrystallization from CHCl<sub>3</sub>, mp 215°C. Found: Ti 13.0; Cl 19.8%.  $C_{16}H_{26}Cl_2Ti$ . Calculated: Ti 13.28; Cl 19.62%. PMR spectrum ( $\delta$ , ppm): 3.45 (4 H), 3.55 (4 H - C<sub>5</sub>H<sub>4</sub>), 7.61 (18 H - C(CH<sub>3</sub>)<sub>3</sub>).

THF (Merck) was purified by the ketyl method [9]. It was kept for several days over NaOH; then it was boiled in an inert atmosphere with metallic Na in the presence of benzophenone until the appearance of the stable dark blue color that is typical of the benzophenone dianion. The solvent was distilled in an inert atmosphere into a special buret with a sample of carefully vacuum-dried support electrolyte. The polarographic cell, with the buret inside it, was evacuated with a solution of support electrolyte, and purged with a stream of dry Ar, after which the solution was poured from the buret into the cell. The sample of test compound was introduced into the cell in an Ar countercurrent. Such a procedure practically eliminates the entrance of air or moisture into the test solutions.

Tetrabutylammonium hexafluorophosphate (Fluka) was the support electrolyte; it was used without further purification at 0.1 M concentration. The reference electrode, to which all potentials were referred, was aqueous saturated calomel electrode, which was separated from the test solution in the cell by a bridge filled with support electrolyte solution. The reference electrode was calibrated with bis(diphenyl)chromium iodide ( $E_{1/2} = -0.68$  V relative to saturated calomel electrode).

Polarograms were recorded with exclusion of the cell by the three-electrode scheme, using a RA-2 polarograph (Czechoslovak SSR). The dropping mercury electrode was equipped with a device for mechanical detachment of the drop ( $t_d = 1.3 \text{ sec}$ ). Measurements were carried out at 20 ± 2°C. Ar was prepurified of traces of oxygen (BTS catalyst) and moisture ( $P_2O_5$ ).

## DISCUSSION OF RESULTS

The polarogram of each complex showed two cathodic diffusion waves of approximately equal height, the half-wave potentials of which are shown  $(E_1/2^1 \text{ and } E_1/2^2)$  in Table 1. From the slopes of the waves (S) (see Table 1) it follows that the electrode processes for both waves are irreversible. From the similarity in polarographic behavior of the unsubstituted complex I [4] and its substituted analogs, it can be presumed that the observed waves correspond to the successive two-electron reductions of the complexes to Ti(III) and Ti(II) derivatives, respectively.

From the effect of substituents on  $E_{1/2}$  the complexes can be arbitrarily divided into two groups: I-III, containing methyl substituents in the ring, and IV-VII, containing alkylidene bridges or bulky tert-butyl substituents.

For the first group, the introduction of substituents into the ring increases the electron density at the metal atom and therefore causes the cathodic shift of  $E_{1/2}^{1}$ ; the amount of the shift increases practically additively with the increase in number of methyl substituents or the sum of their Hammett  $\sigma_{p}$  constants (Fig. 1). Such behavior is also typical of ferrocinium [10] and dibenzochromium [11] cations, and in the general case suggest a purely inductive substituent effect on the TI(IV)  $\rightarrow$  Ti(III) step.

Compound	1st wave			2nd wave			3rd wave		1
	$\begin{bmatrix} -E_{1/2}^{1}, \\ V \end{bmatrix}$	S, mV	i <sub>d</sub> , μΑ	$V^{-E_{1/2}^{2}}$ ,	S, mV	i <sub>d</sub> , μΑ	$V^{-E_{1/2}^{3}},$	i <sub>d</sub> , μΑ	$\Delta E = E_{1/2} - E_{1/2}^2,  \nabla$
(I) (II) (III) (IV) (V) (VI) (VI)	0,86 0,93 1,09 0,85 0,85 0,89 0,91	93 90 83 90 84 90 90 90	1,07 1,02 0,95 0,98 1,02 0,99 0,95	2,10 2,12 2,12 1,95 2,14 2,18 2,07	86 100 72 58 96 138 122	$ \begin{vmatrix} 0,82 \\ 1,10 \\ 1,14 \\ 1,02 \\ 0,77 \\ 0,98 \\ 0,98 \end{vmatrix} $	$\sim 2,4$ 2,79 $\sim 2,6$	~0,2 1,01 ~0,3	1,24 1,19 1,03 1,10 1,29 1,29 1,29 1,16

TABLE 1. Parameters of Polarographic Reduction of Substituted and Bridged Bis(cyclopentadienyl)titanium Dichlorides in THF

$$*S = d(\log i/i_d - i)/dE.$$

Due to the difference in the slopes of the second waves of the complexes, the value  $\Delta E = E_{1/2}^{1} - E_{1/2}^{2}$  is more informative for characterizing the Ti(III)  $\rightarrow$  Ti(II) step; it is typical of the potential region in which the Ti(III) complexes exist. The decrease in  $\Delta E$  in the sequence I > II > III (see Table 1) reflects the increasing ease of addition of the second electron. As with  $E_{1/2}^{1}$ , the value of  $\Delta E$  is linearly related to the number of methyl substituents or to the sum of their Hammet  $\sigma_{p}$  constants (see Fig. 1); however, the increase in electron density at the metal atom does not hinder, but facilitates the transfer of the second electron. This is in complete agreement with the concept of increased stability of substituted titanocenes when the electron donor properties of the stabilizing ligands are increased by the introduction of alkyl substituents into the ring [12].

The appearance in the polarograms of complex III of a third cathodic wave, comparable in height to the first two waves, is apparently related to the increasing stability in the sequence I-III of the most likely products of two-electron reduction, viz., the respective titanocenes. A third wave is also observable for I and IV, but it is poorly defined, and significantly below the level of the one-electron waves (see Table 1). In [4] the appearance of a third wave for  $Cp_2TiCl_2$  is related to the subsequent one-electron reduction of titanocene to the radical anion  $Cp_2Ti^-$ . However, until now this proposal has not received adequate confirmation due to the absence of data on trustworthy electrochemical identification of the electrically generated metastable titanocene. According to the proposal that the third wave is related to the subsequent reduction of titanocene [4], its height must certainly be related to its stability. Since the most stable substituted titanocene is  $(C_5Me_5)_2Ti$  [6], the trustworthy identification of the one-electron reduction of a third polarographic wave for complex III can be considered indirect confirmation of the one-electron reduction of a titanocene of that structure.

For the second group of complexes, IV-VII, the substituent effect on  $E_{1/2}$  is not what would be expected for a purely inductive effect, but is determined primarily by the steric effects of the bulky tert-butyl substituent or the rigid alkylidene bridge. The reason for the effect is not entirely clear, and apparently is different for the tert-butyl and the alkylidene substituents, although in both cases the Ti(IV)  $\Rightarrow$  Ti(III) step is facilitated; this is shown by the anodic shift of  $E_{1/2}$ <sup>1</sup> for complexes IV-VII as compared with I and its methyl-substituted analogs (see Table 1).

It is known [13] that occupation by an electron of the vacant d-orbital of the metal in  $Cp_2ML_2$  complexes significantly decreases the nonvalence contacts between ligands, e.g., in going from  $(MeC_5H_4)_2TiCl_2$  to  $(MeC_5H_4)_2VCl_2$ . It can be presumed that electron transfer to  $Cp_2TiCl_2$  will be easier, the less is the overload of the Ti coordination sphere and correspondingly the mutual repulsion of the ligands and the d electron. The overload of the Ti coordination sphere is easily estimated from structural data, particularly the value of the nonvalent Cl...Cl contact. The overload increases as the Cl...Cl distance decreases in the sequence: V (3.50 Å) > I (3.48 Å) > VI (3.46 Å) > VII (3.44 Å) > II (3.43 Å) > III (3.41 Å) [7, 13-15]. In this sequence the anodic shift of  $E_1/2^{-1}$  appears (see Table 1). This requires the assumption that aside from the electronic effects, the degree of mutual repulsion of ligands in these complexes has a significant effect on  $E_1/2^{-1}$  of the Ti(IV)  $\rightarrow$  Ti(III) step.

As regards the second wave for complexes IV-VII, the anomalously high  $\Delta E$  values for V and VI (see Table 1) reflect the difficulty of the Ti(III)  $\Rightarrow$  Ti(II) step; this is probably related to the need to increase the CpTiCp angle in going to the titanocene structure [16]. For the rigid bridge compounds V and VI this naturally must severally deform the structure and increase the energy level substantially, as shown by the increase in  $\Delta E$ . As the rigidity of



Fig. 1. Dependence of  $E_{1/2}^{1}$  and  $\Delta E = E_{1/2}^{1} - E_{1/2}^{2}$  on sum of Hammett  $\sigma_{\rm p}$  constants of substituents for compounds I-III.

the system decreases and, consequently, the steric hindrance in the sequence V > VI > VII,\* the inductive effect of the substituents begins to appear to a greater extent; in this sequence it leads to the cathodic shift of  $E_{1/2}^{-1}$  and the decrease in  $\Delta E$  that characterize the ease of the Ti(III)  $\rightarrow$  Ti(II) transition. The absence of a third wave in the polarograms of V-VII apparently must be related to the low stability of the corresponding bridged titanocenes. The fact that  $\Delta E$  for IV is lower than should be expected for a purely inductive effect is probably due to steric hindrance, which is also retained in the case of (t-BuC<sub>5</sub>H<sub>4</sub>)<sub>2</sub>TiCl. The transition to the titanocene structure with the large CpTiCp angle must decrease hindrance, so that the reduction of IV to the corresponding titanocene is easier than with the other complexes (see Table 1).

#### CONCLUSIONS

l. Substituted and bridged bis(cyclopentadienyl)titanium dichlorides such as  $Cp_2TiCl_2$ , in THF solution at a dropping mercury electrode undergo stepwise irreversible two-electron reduction.

2. In the absence of steric effects the increase in electron density at the Ti atom when the ring contains alkyl substituents causes first-step  $E_{1/2}$  to shift to the cathodic potential region, and second-step  $E_{1/2}$  to shift to the anodic region.

3. When the ring contains bulky alkyl substituents, or alkylidene bridges that connect the cyclopentadiene ligands, the main influence on  $E_{1/2}$  of the complexes is that of steric effects that facilitate the first reduction step. The rigid alkylidene bridges hinder the second reduction step.

# LITERATURE CITED

- 1. R. E. Dessy, R. B. King, and M. Waldrop, J. Am. Chem. Soc., <u>88</u>, 5112 (1966).
- 2. E. Laviron, J. Besanson, and F. Hug, J. Organomet. Chem., 159, 279 (1978).
- 3. N. El Murr, A. Chaloyard, and J. Tirouflet, J. Chem. Soc. Chem. Communs., 446 (1980).
- 4. Y. Mugnier, C. Moise, and E. Laviron, J. Organomet. Chem., 204, 61 (1981).
- 5. A. N. Nesmeyanova and K. A. Kochetkova (ed.), Methods of Heteroorganic Chemistry. The Copper-Scandium-Titanium-Vanadium-Chromium-Manganese Subgroups. Lanthanides and Actinides [in Russian], Vol. 1, Nauka, Moscow (1974), p. 181.
- 6. J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, J. Am. Chem. Soc., <u>94</u>, 1219 (1972).
- 7. J. A. Smith, J. von Seyerl, G. Huttner, and H. H. Brintzinger, J. Organomet. Chem., <u>173</u>, 175 (1979).
- 8. T. Leigh, J. Chem. Soc., 3294 (1964).
- 9. S. Herzog and J. Dehmert, Z. Chem., 1 (1964).
- 10. S. P. Gubin, Izv. Akad. Nauk SSSR, Ser. Khim., 1551 (1966).
- 11. I. A. Suskina, B. G. Gribov, R. A. Idrisova, L. I. Denisovich, and S. P. Gubin, Izv. Akad. Nauk SSSR, Ser. Khim., 425 (1971).
- 12. H. A. Skinner, Adv. Organomet. Chem., 2, 49 (1964).

\*The CpTiCp angle can serve as measure of rigidity; it increases in this sequence from 121 to 133 deg [7].

13. J. L. Peterson and L. F. Dahl, J. Am. Chem. Soc., 97, 6422 (1975).

- 14. B. R. Davis and I. Bernal, J. Organomet. Chem., <u>30</u>, 75 (1971).
- 15. T. C. McKenzie, R. D. Sanner, and J. E. Bercaw, J. Organomet. Chem., 102, 457 (1975).

 R. D. Sanner, D. M. Duggan, T. C. McKenzie, R. E. Marsh, and J. E. Bercaw, J. Am. Chem. Soc., <u>98</u>, 8358 (1976).

STEREOSPECIFICITY OF SPIN-LATTICE RELAXATION TIMES COMMUNICATION 3. LONGITUDINAL RELAXATION OF **PROTONS**, DIPOLE MOMENTS, <sup>13</sup>C NMR SPECTRA, AND CONFORMATIONS OF DIASTEREOMERIC PHTHALYL ACÉTALS

 R. Kh. Sadykov, E. N. Klimovitskii,
 UDC 541.67:541.63:543.

 Yu. Yu. Samitov, and B. A. Arbuzov
 422.25:547.584

It is known that the presence of conformational equilibrium of the chair and twist forms is generally characteristic of 1,3-dioxacyclohept-5-enes and their 5,6-dichloro and benzo derivatives [1-6]. The relative position of conformational equilibrium is essentially a function of the steric volume of the substituent at  $C^2$  [3]. The most cumbersome of these compounds, t-Bu, which is subject to maximum stress in the elastic form, executes the role of a binding group and shifts the equilibrium toward the chain conformation only in the phthalyl acetal series [1, 6] (compare [3, 4]).

 $_{C-T}^{C-T}$  The conformational energy of the C(CH<sub>3</sub>)<sub>3</sub> group in the 1,3-dioxacyclohept-5-ene series,  $\Delta H_{t-Bu}^{C-T}$  was determined to be  $\ll 2.0$  kcal/mole by the method of IR spectroscopy [6]. If we assume that the value of  $\Delta H_{t-Bu}^{C-T}$  remains close to this value in the phthalyl acetal series, it is possible to predict that introduction of an axial substituent in position 4 (7) of 2-tert-butylbenz[e]1,3-dioxepan would create the conditions for the appearance of elastic conformations. It was shown in [7, 8] that the chair form is the only experimentally observed form in the presence of axial CH<sub>3</sub> and Ph groups. Based on the information obtained, it was suggested that an axial substituent at C<sup>4</sup> (C<sup>7</sup>) would deform the chair conformation.

Seven-member acetals of this type do not contain any stereochemical fragments whose analysis by traditional methods of NMR spectroscopy would permit judging such a fine conformational effect as deformation of the chair form. The proton spin-lattice relaxation of diastereomeric phthalyl acetals (I)-(IV), including model compounds (V)-(VI)



was studied to obtain this information.

It was first reasonable to assign the two  $H_{\alpha}$  and  $H_{e}$  quartets and the corresponding doublets of the  $CH_{3}$  groups in the <sup>1</sup>H NMR spectrum of acetal (II) [7]. The approach for this assignment was based on the mechanisms caused by stereospecificity of the first type. The concept of the stereospecificity of nuclear magnetic relaxation times is described in [9, 10]. It should be assumed that stereospecificity of the first type is due to a dipole interaction, \*Communication 3 of the series "Stereochemistry of Seven-Member Heterocycles."

A. M. Butler Chemical Institute. V. I. Ul'yanov-Lenin Kazan State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2497-2502, November, 1983. Original article submitted April 5, 1983.

0568-5230/83/3211-2245\$07.50 © 1984 Plenum Publishing Corporation

2245