## Peculiarities of the reaction of 2,2,6,6-tetramethylpiperidin-1-oxyl with Cp<sub>2</sub>TiEtCl

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The reaction of 2,2,6,6-tetramethylpiperidin-1-oxyl (1) with Cp<sub>2</sub>TiEtCl (2) has been studied. The consumption of 1 and evolution of gaseous products (ethane, ethylene) proceed with autoacceleration. Increasing the 1:2 molar ratio leads to inhibition of the autoacceleration. The fact that the yield of ethane is higher than that of ethylene indicates that the reaction proceeds via S<sub>R</sub>2 substitution of the ethyl group in Cp<sub>2</sub>TiEtCl for radical 1. The mechanism of the substitution is synchronous. A kinetic model of the reaction has been proposed and substantiated.

Key words: dicyclopentadienyltitanium(iv) ethylcloride, 2,2,6,6-tetramethylpiperidin-1-oxyl, kinetics, S<sub>R</sub>2 substitution, ESR spectroscopy.

The results of our previous studies testify that nitroxyl radicals form complexes with transition metal  $(TiCl_4, TiCl_3, VOCl_3, VCl_2, VCl_2, WCl_6, and MoCl_5)^1$ and organoaluminum compounds.<sup>2,3</sup> In many cases, the complexes undergo further transformations. The elucidation of the possibility and directions of these transformations, using relatively simple model systems as examples, is of interest for understanding the details and specific features of the mechanisms of the various processes catalyzed by transition metal complexes and Lewis acids as well as of the inhibition of polymerization and other reactions.

The reaction of 2,2,6,6-tetramethylpiperidin-1-oxyl (1) with  $Cp_2TiEtCl$  (2) is studied in the present work.

## Experimental

The kinetics of consumption of the piperidinoxyl radical 1 in the presence of 2 was studied by the ESR method on an EPR-2 spectrometer (Design Bureau of the Institute of Chemical Physics in Chernogolovka, RAS). The reaction was carried out in an argon atmosphere in a flask with an outlet placed in a resonator of the instrument with a thermostating attachment. The yield of gaseous products (GP) was determined on a glass vacuum installation by the volumetric method. The composition of GP and reaction products in the liquid phase was determined by GLC on an LKhM-8MD chromatograph according to a standard procedure (column 2 m, stationary phase: for analysis of gases, 5% Apiezon L on Al<sub>2</sub>O<sub>3</sub> (A-1 trade mark), diameter of particles 0.25-0.50 mm; for analysis of liquid-phase products, Chromaton N-AW, 5% SE-30, size of particles 0.20-0.25 mm). Complex 2 was synthesized by a known method,<sup>4</sup> m.p. 365-367 K. Nitroxyl radical 1 was obtained by a procedure described previously in Refs. 1-3and purified by sublimation in vacuo. The solvents were purified by standard methods and distilled in an argon atmosphere. The titanium piperidinoxyl derivative  $Cp_2Ti(ONC_9H_{18})Cl$  was synthesized by the reaction of equimolar amounts of 2 and radical 1 in toluene at 345 K for 3 h after distilling off volatiles. Found (%): C, 65.7; H, 8.6; Ti, 12.75; Cl, 9.43.  $C_{19}H_{28}TiCION$ . Calculated (%): C, 61.72; H, 7.58; Ti, 12.97; Cl, 9.61.

## **Results and Discussion**

The reaction of 2 with radical 1 occurs at a noticeable rate only at temperatures above 333 K. The kinetics of the consumption of radical 1 in the reaction at 345 K at different concentrations of 2 is presented in Fig. 1. It can be seen that at the ratios 1 : 2 = 0.5-1.0 the radicals are almost completely consumed. With a twofold excess of radical 1 with respect to 2, ~1.5 moles of radical 1 per mole of the initial compound 2 is consumed in the reaction. When the concentration of 2 is equal to 2.6-3.0 mmol L<sup>-1</sup> and the ratio 1 : 2 is equal to 0.1-2.0, the reaction in toluene is completed in 15-60 min at 345 K. The shapes of the kinetic curves indicate that the consumption of the radical 1 during the transformation at 333-353 K has an autocatalytic character.

If other conditions remain unchanged, the duration of the induction period of the kinetics of consumption of radical 1 shortens when the temperature increases, when the concentration of 2 increases (*i.e.*, when the molar ratio 1 : 2 decreases), when the initial concentrations of both reagents increase simultaneously, and under photoirradiation. Radical 1 is consumed without an induction period in pyridine as well as at temperatures above 363 K in toluene and decalin. GP are formed

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Solvent	T/K	[ <b>2</b> ] <sub>0</sub>	[ <b>1</b> ] <sub>0</sub>	t/h	Q (mol.% of [2] <sub>0</sub> )			
		/mmol L <sup>-1</sup>	[ <b>2</b> ] <sub>0</sub>		$C_2H_4$	$C_2H_6$	ROEt*	ROH*
Toluene	353	27.0	1	1	15	35	27	_
Toluene	353	26.9	1	1	10	33	27	_
Toluene	353	26.6	0.5	1	15	20	9	_
Toluene (P)**	293	51.3	1	4.5	18	47	24	7
Pyridine	343	76.0	2	1	9	12	36	_
Pyridine	353	26.9	1.4	1	5	13	15	3

Table 1. Yield (Q) and composition of products of the reaction of 2 with 1

\*  $R = C_9 H_{18} N$ . \*\* P is photolysis.

during the reaction. In toluene at 343 K, they are evolved with an induction period, whose duration corresponds to that of the induction period of the kinetics of consumption of radical 1.

When the reaction was performed in toluene and pyridine at ratios 1 : 2 > 1.0, titanium(111) was not found in the reaction products by the ESR method. At the ratio 1 : 2 = 1.0, Cp<sub>2</sub>TiCl was found in the solution by the ESR method (g-factor 1.9775) 2 h after the complete consumption of radical 1 at 353 K. Its appearance in the reaction products under these conditions can be explained by the thermal decomposition of unreacted 2.

To obtain data on the mechanism of the reaction of radical 1 with 2, the composition of gaseous and liquid reaction products was studied (Table 1). The overall yield of GP depends on the nature of the solvent, the duration of the reaction, and temperature. When the reaction occurs in toluene at 343-353 K for 1.5-3.0 h, 0.1-0.6 moles of GP per mole of the initial compound 2 is liberated. No more than 0.3 moles of GP per mole of the initial compound 2 is formed after 3 h in pyridine under the same conditions. The GP consist of ethane (~70-80 vol.%) and ethylene (~20-



Fig. 1. Kinetics of consumption of radical 1 (5 mmol  $L^{-1}$ ) in its reaction with 2 in toluene at 345 K and at a [1] : [2] ratio equal to 2.0 (1); 1.0 (2); and 0.5 (3).

30 vol.%). No butane was found in the reaction products or the products of alcoholysis of the reaction mixture. These observations testify that the ethylene formed does not undergo insertion into the Ti-C bond in unreacted 2 and the recombination of ethyl groups (or ethyl radicals) does not occur.

It was observed that the content of ethylene in GP decreases when the reaction occurs in Tetralin (from 33 vol.% 10 min after the beginning of the reaction to 13 vol.% 70 min after the beginning of the reaction). In octadeuterotoluene (ODT), monodeuteroethane (up to 25 mol.% of the total content of ethane in GP) is formed along with ethane and ethylene. This testifies that ODT is involved in the reaction.

Ethoxy-2,2,6,6-tetramethylpiperidine-1 (14-36 mol.% of the initial compound 2) and, in some experiments, hydroxy-2,2,6,6-tetramethylpiperidine-1 (3-7 mol.% of the initial 2) were observed in the solution by GLC. The yield of the latter compound increases to 16.7 mol.% when the reaction mixture is treated with ethanol. This fact can be explained by the partial replacement of the 2,2,6,6-tetramethylpiperidin-1-oxyl groups bound to titanium by ethoxyl groups.

The yields of GP and  $EtONC_9H_{18}$  depend on the ratio of the reagents. When the 1 : 2 ratio is equal to  $1\Omega$ , ~48 mol.% GP containing 69% ethane and 31% ethylene are formed. If other conditions remain unchanged, the yield of GP decreases when using excess 2 and especially excess 1. By contrast, the yield of the ester  $EtONC_9H_{18}$  increases monotonically as the molar ratio 1 : 2 increases (Table 2).

The data of Table 2 show that when the yields of all products of the reaction of radical 1 with 2 in toluene are taken into account, a satisfactory balance with re-

**Table 2.** Dependences of yields of ester  $EtONC_9H_{18}$  and GP on the molar ratio 1:2

Ratio 1 : 2	$EtONC_9H_{18}$ : 2	Yield of GP (mol.% of 2)		
0.5	0.09	35		
1	0.27	50		
2	0.32	10		

spect to the number of ethyl groups introduced into the reaction as complex 2 is achieved.

Similar products are also formed during the photolysis of 2 in toluene at 293 K in the presence of the equimolar amount of radical 1.

After the reaction was completed, a titanium compound with the composition  $(C_5H_5)_2Ti(ONC_9H_{18})Cl$ (3) (according to the results of elemental analysis) was isolated from the solution.

It has been established by the ESR method for the reaction of radical 1 with 2 in toluene and pyridine that the splitting constant,  $a_N$ , on the nitrogen atom of radical 1 in the presence of 2 virtually does not differ from the  $a_N$  value in the absence of 2 ( $a_N \approx 15.6$  Oe). At the same time, the spectrum (in the visible range) of a solution of an equimolar mixture of both components in toluene at 293 K is almost the same as that of a solution of 2. The differential analysis of the spectra of these solutions revealed no new absorption bands in the visible spectral region. Therefore, the concentration of intermediate Cp<sub>2</sub>TiEtCl· $nONC_9H_{18}$  complexes is negligible.

The character of the dependence of the yields of the ester and GP on the ratio of the initial reagents, the participation of the solvent in the reaction, and the considerably higher yield of ethane over that of ethylene make it possible to assume the following mechanism of the initial stage of the process (reactions (1)-(8)).

$$\begin{array}{ccc} Cp_2 TiEtCl + C_9 H_{18} NO^{\cdot} & \longrightarrow \\ 2 & 1 \\ & \longrightarrow & Cp_2 Ti(ONC_9 H_{18})Cl + Et^{\cdot} \end{array}$$
(1)

$$\begin{array}{c} Cp_2 TiEtCl + Et & \longrightarrow & Cp_2 TiCl + C_2 H_4 + C_2 H_6 \end{array} (2) \\ \textbf{2} \end{array}$$

$$Et^{\prime} + C_0 H_{10} NO^{\prime} \longrightarrow EtO - NC_9 H_{18}$$
(3)

$$1 \qquad \qquad C_2H_4 + HO_NC_9H_{18} \quad (4)$$

 $Et' + PhCH_3 \longrightarrow PhCH_2' + C_2H_6$ (5)

$$Cp_2TiEtCl + PhCH_2 \longrightarrow Cp_2TiCl + C_2H_4 + PhCH_3$$
 (6)  
2

$$PhCH_{2} + C_{9}H_{18}NO^{*} \longrightarrow PhCH_{2} - ONC_{9}H_{18}$$
(7)

$$Cp_{2}TiCI + C_{9}H_{18}NO^{-} \longrightarrow Cp_{2}Ti(ONC_{9}H_{18})CI \qquad (8)$$
1

Reaction (1) is an example of the homolytic  $S_R^2$  substitution of the ethyl group for radical 1 in the coordination sphere of titanium. In the case of 2 at 343–353 K, this is the main direction of the transformation, because the act of homolytic substitution is energetically favorable.<sup>5</sup> The determining significance of reaction (1) is confirmed by the fact that the content of

ethane in the reaction products is approximately 3 times higher than the content of ethylene. This conclusion follows from the analysis of the alternative scheme including the reactions of disproportionation (9) and recombination (10) of radical  $\mathbf{1}$  with the ethyl group of  $\mathbf{2}$ in the coordination sphere of the titanium atom.

$$Cp_{2}TiEtCI + C_{9}H_{18}NO'$$

$$2 1 Cp_{2}TiCI + EtONC_{9}H_{18} (9)$$

It is likely that the role of these reactions in the overall reaction of radical 1 with 2 is insignificant, because a slight amount of  $HONC_9H_{18}$  was observed in the products, and ethane rather than ethylene is the main GP.

The absence of the formation of a complex between radical 1 and 2 probably testifies that reaction (1) proceeds via the mechanism of synchronous substitution. The *tert*-butoxyl radical reacts in the same way with dialkylplatinum complexes<sup>6</sup> and alkylboron and -tin derivatives.<sup>7</sup>

The ethyl radical formed in reaction (1) can further react with compound 2, radical 1, and toluene (reactions (2)–(5), respectively). The relative contribution of these reactions is determined by the rate constants and concentrations of the corresponding reagents. The exact values of the rate constants of reactions (2)–(4) are unknown. According to our data,<sup>8</sup>  $k_2 \approx 10^6$  L mol<sup>-1</sup> s<sup>-1</sup> at 353 K. The  $k_3$  and  $k_4$  values can range from  $10^7$  to  $10^8$  L mol<sup>-1</sup> s<sup>-1</sup>.<sup>9</sup> Taking into account the known data on the  $k_{rec}/k_{dispr}$  ratio,<sup>10</sup> it can be accepted that  $k_4$ should be several times lower than  $k_3$ . Due to the high



Fig. 2. Effect of products of the reaction of radical 1 with 2 obtained *in situ* on the duration of the induction period at 345 K in toluene. [1] = [2] = 5 mmol L<sup>-1</sup>. Concentration of reaction products: 0 (1); 1.7 (2); 2.5 (3); and 3.5 (4) mmol L<sup>-1</sup>.



Fig. 3. Effect of products of the reaction of radical 1 with 2 at 345 K in toluene on the duration of the induction period. [1] = [2] = 5 mmol L<sup>-1</sup>. Added reaction products: *1*, no products; *2*, volatiles (EtONC<sub>9</sub>H<sub>18</sub>); and *3*, nonvolatiles (Cp<sub>2</sub>Ti(ONC<sub>9</sub>H<sub>18</sub>)Cl).

value of  $k_3$ , a portion of the ethyl radicals formed in reaction (1) probably recombines with radical 1 to form ethoxy-2,2,6,6-tetramethylpiperidine-1. However, it cannot be ruled out that some fraction of this compound can be formed by the intrasphere recombination of radical 1 with the ethyl group of complex 2.

At 353 K,  $k_5 \approx 10^3$  L mol<sup>-1</sup> s<sup>-1</sup>.<sup>10</sup> The experimental data show that reaction (5) has a noticeable effect on the composition and yield of GP.

One-electron oxidation (8) of titanium(11) by radical 1 occurs at a high rate,<sup>1</sup> therefore  $Cp_2TiCl$  is not accumulated in the products. The high rate of this reaction was confirmed by the ESR method for the  $Cp_2TiCl$ -radical 1 system.<sup>1</sup>

It was shown in special experiments (Fig. 2) that an increase in the rate of consumption of radical 1 during the transformation (autoacceleration) is caused by the reaction products formed *in situ*. Volatiles (ester EtONC<sub>9</sub>H<sub>18</sub>) as well as titanium piperidinoxyl derivative 3, which was isolated by distilling off the solvent and ester EtONC<sub>9</sub>H<sub>18</sub>, have almost no effect on the duration of the induction period and the shapes of the kinetic curves of the consumption of radical 1 during the reaction (Fig. 3).

The autocatalysis that occurs during the transformation can be explained by assuming that compound 2forms fairly stable complexes with the titanium-containing reaction product 3 (reaction (11)) and that the formation of this complex results in the activation of the ethyl group bound to the titanium atom. This likely facilitates the homolytic substitution of the ethyl group for the nitroxyl radical 1 in reaction (12).



Fig. 4. Effect of the initial concentrations of compound 2 and radical 1 on the kinetics of consumption of 1. Toluene, 345 K. [1] = [2]. [1]<sub>0</sub> = 2.7 (*I*); 5.0 (2); and 10.0 (3) mmol  $L^{-1}$ .

$$\mathbf{2} + \mathbf{3} \quad = \quad \mathbf{C} \mathbf{p}_2 \mathsf{T} \mathsf{i} \mathsf{E} \mathsf{t} \mathsf{C} \mathsf{l} \cdot \mathsf{C} \mathbf{p}_2 \mathsf{T} \mathsf{i} (\mathsf{ONC}_9 \mathsf{H}_{18}) \mathsf{C} \mathsf{l} \tag{11}$$

$$Cp_2TiEtCl \cdot Cp_2Ti(ONC_9H_{18})Cl + 1 \longrightarrow 2 Cp_2Ti(ONC_9H_{18})Cl + Et$$
(12)

 $\mathbf{3} + \mathbf{1} \quad \mathbf{C} \mathbf{p}_2 \mathsf{T} \mathsf{i} (\mathsf{ONC}_9 \mathsf{H}_{18}) \mathsf{C} \mathsf{i} \cdot \mathsf{ONC}_9 \mathsf{H}_{18} \tag{13}$ 

Increasing the concentration of compound 3 during the reaction results in a progressive increase in the rate of consumption of radical 1. This conclusion is confirmed by the fact that the maximum rate of consumption of radical 1 (rate of autoacceleration) increases as the initial concentrations of both reagents increase (Fig. 4).

The self-association of compound 3 (*i.e.*, intermolecular complex formation at the donor and acceptor centers of a molecule) that occurs in isolation as well as the formation of complexes of this compound with radical 1 (reaction (13)) when the molar ratio 1 : 2increases results in the formation of adducts that are probably inert with respect to 2. It can be assumed that this is precisely the reason for the "inhibition" of the autocatalysis by nitroxyl radical 1 and for the insignificant effect of the additions of preliminarily isolated compound 3 on the rate of consumption of radical 1.

Since the complex of 3 with 2 favors the acceleration of the process, the decrease in the concentration of 3 due to its formation of a complex with 1 (reaction (13)) manifests itself as an inhibition of autoacceleration by the complex of 3 with 1. In other words, compound 3 is likely the strongest Lewis acid in the system considered. Compounds 1 and 2 are weak Lewis bases with respect to 3. Therefore, both 1 and 2 are involved in reversible complex formation with 3 (reactions (11) and (13)).

The formation of complexes of the initial reagents with compound 3 was confirmed by spectrophotometry.

It was established by the differential method that the complex of radical 1 with compound 3 absorbs in the region of 440 nm, and the complex of 2 with 3 absorbs at 456 nm.

The decrease in the concentrations of 1 and 2 during the reaction and blocking of the coordination site at the titanium atom<sup>4</sup> in 2 by compound 3 result in a decrease in the rates of reactions (2) and (4); due to this a considerable portion of the ethyl radicals formed in the reaction reacts with the solvent (reaction (5)). The latter manifests itself as an increase in the fraction of ethane in the GP that are evolved at the later stages of the transformation, and as the formation of EtD when the reaction occurs in ODT.

It was established in blank experiments that the thermolysis of 2 in toluene to form Cp<sub>2</sub>TiCl and ethyl radicals occurs at a very low rate under the conditions studied. As a result, the kinetics of the process and the composition of the products formed can be explained from the scheme including the reactions considered above. By contrast, the rate of thermolysis of 2 in pyridine is high  $(k = 3 \cdot 10^{-3} \text{ s}^{-1} \text{ at } 353 \text{ K}).^{11}$  This means that the reaction of radical 1 with 2 in pyridine is complicated or is determined by the parallel thermal decomposition of 2.

It should be mentioned in conclusion that the formation of ethylene and ethoxy-2,2,6,6-tetramethylpyperidine-1 in a ratio close to unity in the reaction of radical 1 with 2 may indicate that the reactivities of the ethyl group of 2 and radical 1 with respect to the ethyl radical are comparable.

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