Electroactive Protecting Groups and Reaction Units, 6[◇]

Titanium Enolate Radical Cations in Solution: Generation, Characterization, and Their Reactions

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Received November 28, 1996

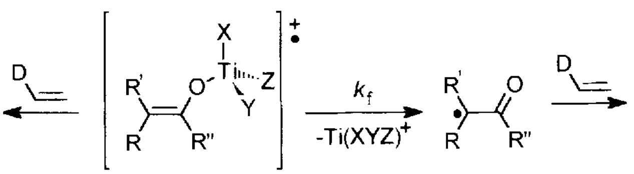
Keywords: Titanium enolate / Cyclic voltammetry / EPR spectroscopy / Radical ion / Mesolytic bond cleavage

For the first time, titanium enolate radical cations were characterized in cyclic voltammetry experiments. Preparative one-electron oxidation of titanium enolates **1**–**3** led to the formation of benzofurans **B1**–**B3** through mesolytic Ti–O bond fragmentation to α-carbonyl radical and a cationic titanocene(IV) species. With $\mathbf{1}^{+\bullet}$, the kinetics of the Ti–O bond cleavage was investigated by fast scan cyclic voltammetry providing a first-order rate constant $k_f = 850 \pm 50\ s^{-1}$ in acetonitrile at room temperature. The titanium enolate radical cations $\mathbf{1}^{+\bullet}$, $\mathbf{3}^{+\bullet}$, $\mathbf{4}^{+\bullet}$ and $\mathbf{5}^{+\bullet}$ were characterized by EPR spectroscopy, qualifying these species as electrophilic radicals. This feature can be exploited in C–C bond formation reactions such as the formal dimerization of **6** to 2,3-dimethyl-1,4-diphenylbuta-1,4-dione **D6**, which takes place on stage of the radical cation $\mathbf{6}^{+\bullet}$.

Increasingly, titanium compounds play a decisive role as catalysts or reagents in important organic transformations[2], e.g. such as the Ziegler-Natta polymerization[3], McMurry reaction[4], the Sharpless epoxidation[5], and stereoselective aldol additions via titanium enolates[6]. The main advantage of titanium enolates over the usual lithium enolates is the possibility to carry out their reactions enantioselectively by incorporating chiral ligands at the metal center[7]. In addition, they have also been used in stereoselective Michael reactions[8] as well as in oxidations with oxygen-transfer reagents[9]. Surprisingly, the umpolung of the nucleophilic titanium enolates by one-electron oxidation is so far unknown, although such radical cations should offer interesting electrophilic features that could be exploited in carbon–carbon bond formation, quite in analogy to the recent chemistry of silyl[10] and stannyl[11] enol ether radical cations.

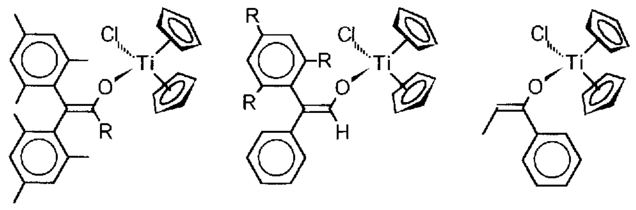
In order to use titanium enolates in oxidative enantioselective reactions (with a chiral auxiliary at the titanium atom) C–C bond formation has to take place at the stage of the chiral radical cation. If the lifetime of this electrophilic species is too short because of fast Ti–O bond cleavage (k_f), only achiral α-carbonyl radical intermediates will be the decisive species in the bond formation process. Hence, C–C bond formation has to be faster than the Ti–O bond rupture.

Scheme 1. Conceivable reaction pathways of the titanium enolate radical cations; D = donor



As a consequence, we have now started an investigation on the one-electron oxidation of titanium enolates[12] and the properties of such electrophilic odd-electron species. This investigation relies heavily on the availability of pure and stable titanium enolates, a prerequisite which is not easy to fulfill, because titanium enolates are known as reactive and moisture sensitive species. It is well-known that only few titanium enolates have been isolated[13]. By using simple stable enols as precursors we were able to synthesize a series of titanium enolates which exhibit an exceptional stability towards hydrolysis[14] and additionally should be adequate model compounds for one-electron oxidation studies.

Scheme 2. Model compounds



1: R = H
2: R = *t*Bu
3: R= Ph

4: R = CH$_3$
5: R = H

6

[◇] Part 5: See ref.[1].

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Results

All model compounds showed irreversible oxidation potentials in the range of 0.30–0.54 V *vs.* ferrocene/ferrocenium[15] at 100 mV s^{-1} in acetonitrile as determined by cyclic voltammetry (CV) (see Table 1). This is within an excellent range where chemical one-electron oxidation of the titanium enolate electrophore system can be selectively realized in the presence of many other common functional groups. At higher scan rates fully reversible waves could be obtained for **1** ($\nu \geqslant 20$ V s^{-1}), for **2** and **3** ($\nu \geqslant 500$ mV s^{-1}) and for **5** ($\nu \geqslant 750$ V s^{-1}) in dichloromethane. This represents the first direct observation of titanium enolate radical cations in an electrochemical experiment, allowing for the determination of the thermodynamically relevant redox potentials $E_{1/2}$ (see Table 1). For **6** no sign of reversibility could be monitored even at scan rates up to 40000 V s^{-1} in dichloromethane.

Table 1. Oxidation potentials of the titanium enolates determined by CV

Titanium Enolate	E_{pa} [V *vs.* Fc]	$E_{1/2}$ [V *vs.* Fc]
1	+ 0.44[a]	+ 0.50[b]
2	+ 0.30[a]	+ 0.26[c]
3	+ 0.38[a]	+ 0.31[c]
4	+ 0.44[a]	
5	+ 0.40[a]	+ 0.49[d]
6	+ 0.54[a]	

[a] In acetonitrile at v = 100 mV s^{-1}. – [b] In dichloromethane at v = 100 V s^{-1}. – [c] In dichloromethane at v = 100 mV s^{-1}. – [d] In dichloromethane at v = 1000 V s^{-1}.

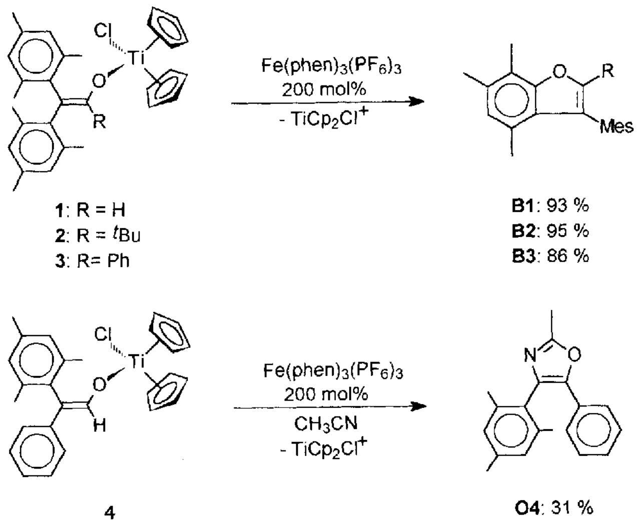
The preparative one-electron oxidations of the sterically congested titanium enolates **1**–**3** with 200 mol% of tris(1,10-phenanthroline)iron(III)hexafluorophosphate [Fe(phen)$_3$](PF$_6$)$_3$ ($E_{1/2}$ = +0.76 V) as an outer-sphere one-electron oxidant in acetonitrile or an acetonitrile/dichloromethane 1:1 mixture (as in the case of **2**), afforded the benzofuran derivatives **B1**–**B3** (Scheme 3) in very good yields. In contrast, the one-electron oxidation of **4** with 200 mol% [Fe(phen)$_3$](PF$_6$)$_3$ in acetonitrile led to the oxazole derivative **O4** and not to the benzofuran **B4**.

The sterically least shielded titanium enolate **6** undergoes a formal dimerization reaction to 2,3-dimethyl-1,4-diphenylbuta-1,4-dione (**D6**) (*meso*: *D*/*L* = 1:1) after one-electron oxidation, which represents the only detectable product of this reaction.

In standard CV investigations of **1**–**3** two additional oxidation waves appear at higher anodic potentials besides the oxidation wave of the titanium enolates (wave I). These waves could be readily assigned to the oxidation of the corresponding enols (wave II) and the oxidation of the benzofuran derivatives (wave III) by comparison of their potentials with electrochemical data obtained from authentic samples[16d].

In multisweep CV experiments in acetonitrile, the current for wave I rapidly decreases with increasing number of scans, while the currents for wave II and III grow relatively to that for wave I. This observation suggests a conversion of the titanium enolates into the corresponding enols and the benzofuran derivatives **B1**–**B3** already on the time scale of the CV experiment.

Scheme 3



Scheme 4

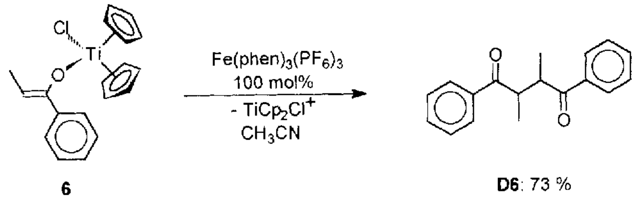
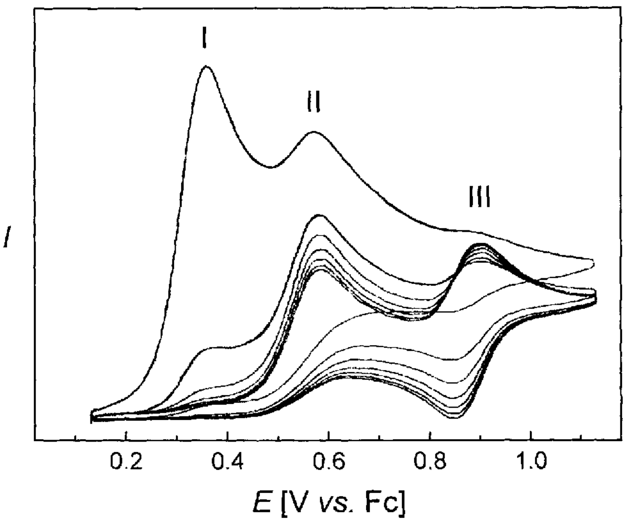


Figure 1. Multisweep CV of **3** in acetonitrile at v = 200 mV s^{-1} containing 0.1 M Bu$_4$NPF$_6$



After addition of di-*tert*-butylpyridine as a non-nucleophilic base, wave II decreased in height and finally vanished completely (after addition of 20 equivalents). In contrast, stoichiometric addition of trifluoromethanesulfonic acid immediately led to the quantitative protolytic cleavage of the titanium enolate **1** as demonstrated by the appearance

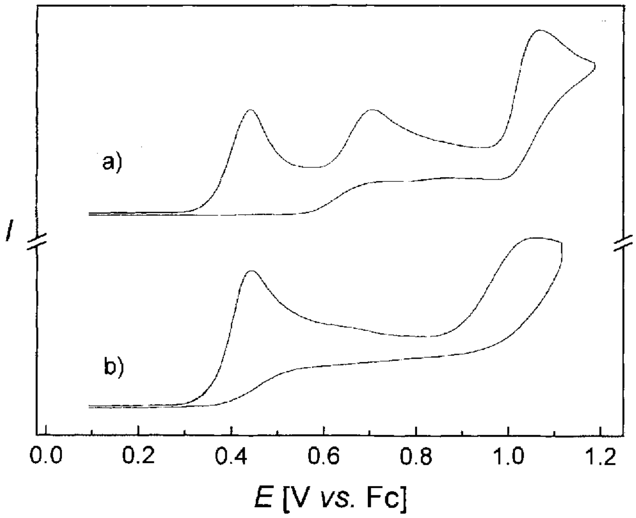
Table 2. Redox potentials of the corresponding enols **E1**−**E3** and benzofuran derivatives **B1**−**B3** in acetonitrile at v = 100 mV s^{-1} containing 0.1 M Bu_4NPF_6[16]

Enol	E_{pa} [V *vs.* Fc]	Benzofuran	$E_{1/2}$ [V *vs.* Fc]
E1	+0.67	**B1**	+1.06[a]
E2	+0.64	**B2**	+0.93
E3	+0.60	**B3**	+0.87

[a] Anodic peak potential.

of the new wave at E_{pa} = +0.67 V, which could be unambiguously assigned to the electrochemically well-characterized enols[16].

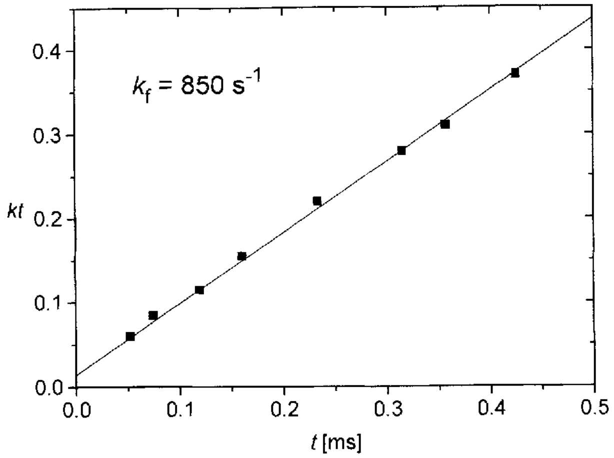
Figure 2. CV of **1** in acetonitrile at v = 100 mV s^{-1}; a) without addition; b) in presence of 20 equivalents of di-*tert*-butylpyridine



In order to determine the kinetics of the titanium enolate radical cation reaction it was necessary to suppress the protolytic cleavage of neutral titanium enolate because the formed enol would be able to undergo rapid intermolecular electron transfer reactions with the titanium enolate radical cation. For this reason, we added 20 equivalents of 2,6-di-*tert*-butylpyridine as a non-nucleophilic base, and, indeed, enol formation on the time scale of the CV experiment was suppressed. Using fast-scan CV at ultramicroelectrodes of 25 μm diameter (Au) and scan rates between 200 and 3000 V s^{-1} partially reversible waves of the titanium enolate were obtained upon oxidation. From the ratio of cathodic to anodic peak current I_{pc}/I_{pa} the kinetic parameter kt was evaluated according to the method of Nicholson and Shain[17] by applying a working curve for an $EC_{irr}E$ mechanism (electron transfer / chemical reaction / electron transfer). The working curve had been obtained from digital simulation of cyclic voltammograms using the implicit Crank-Nicholson technique[18] with parameters obtained from CV measurements of **1**. This kinetic investigation provided a first order-rate constant of $k_f = 850 \pm 50\ s^{-1}$ for the mesolytic[19] bond cleavage of $\mathbf{1}^{+\bullet}$.

The kinetics of this bond scission reaction is slowed down in dichloromethane by about a factor of 1000 compared to acetonitrile. Unfortunately, the exact determination of the rate constant in dichloromethane failed due to rapid electrode coating after addition of base. Thus, the lifetime of the radical cation $\mathbf{1}^{+\bullet}$ in dichloromethane was approximated from measurements without base at room temperature. Since a reduction wave appeared at scan rates $v \geqslant 100$ mV s^{-1} the first-order rate constant can reliably be estimated to $k_f < 1\ s^{-1}$. By comparison, radical cations $\mathbf{2}^{+\bullet}$ and $\mathbf{3}^{+\bullet}$ exhibit somewhat longer lifetimes as indicated by the higher reversibility in the cyclic voltammograms in dichloromethane.

Figure 3. Kinetics of the mesolytic bond cleavage of $\mathbf{1}^{+\bullet}$; v = 200−3000 V s^{-1}, 0.02 M in acetonitrile containing 0.2 M Bu_4NPF_6



At even higher scan rates, when fully reversible waves were obtained (vide supra), neither the oxidation of the corresponding enol (wave II) nor the benzofuran (wave III) could be observed in the electrochemical experiment of titanium enolates **1**−**3** (both in acetonitrile and dichloromethane).

Due to the comparatively long lifetimes of the titanium enolate radical cations we were able to record EPR-spectra of $\mathbf{1}^{+\bullet}$, $\mathbf{3}^{+\bullet}$−$\mathbf{5}^{+\bullet}$ in dichloromethane at −100°C. These species were generated by one-electron oxidation of the neutral precursor with tris(*p*-bromophenyl)aminium hexachloroantimonate ($E_{1/2}$ = +0.70 V). The radical cations $\mathbf{1}^{+\bullet}$, $\mathbf{3}^{+\bullet}$ and $\mathbf{4}^{+\bullet}$ were persistent for several hours whereas the EPR signal for $\mathbf{5}^{+\bullet}$ decayed within one hour under these conditions. EPR-detection of $\mathbf{2}^{+\bullet}$ failed because of insufficient solubility of the neutral titanium enolate **2**. Unfortunately, for $\mathbf{1}^{+\bullet}$ and $\mathbf{3}^{+\bullet}$ only unresolved spectra could be obtained in spite of varying the concentration, while for $\mathbf{4}^{+\bullet}$ hyperfine splitting caused by vinyl, phenyl and mesityl hydrogen atoms is observed. The digital simulation is in good agreement with the experiment; the parameters used are shown in Figure 4.

Discussion

Oxidative formation of benzofurans **B1**−**B3** from simple, stable enols and from various other enol derivatives[20−23] is known to proceed via an intermediate α-carbonyl cation which undergoes cyclization, [1,2]-methyl shift and deprotonation. In all these oxidations mesolytic bond cleavage constitutes the key reaction.

Table 3. g-Values of titanium enolate radical cations

Radical cation	g value
$1^{+\bullet}$	2.0043
$3^{+\bullet}$	2.0029
$4^{+\bullet}$	2.0036
$5^{+\bullet}$	2.0038

Figure 4. EPR-spectrum of $4^{+\bullet}$ and digital simulation

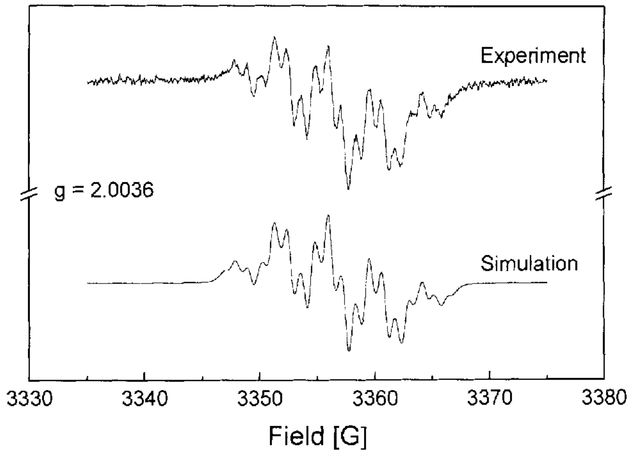


Table 4. Parameters used for digital simulation of the EPR spectrum of $4^{+\bullet}$

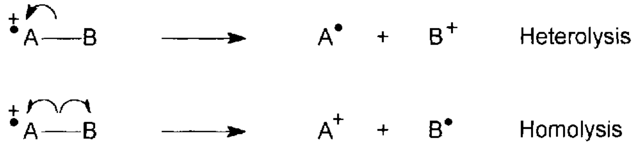
a^H [G]		
4.82	1 H	C=C-H
3.44	3 H	*o-/p*-Ph-H
1.23	2 H	*m*-Ph-H
0.84	2 H	*m*-Mes-H
0.10	9 H	Mes-CH_3

Mesolytic Bond Cleavage

In the case of titanium enolates **1**–**3** as well, Ti–O bond cleavage must have taken place somewhere in the course of the oxidative benzofuran formation, but we still have to identify the corresponding reaction step. It is fortunate for the mechanistic interpretation that a direct cyclization on the stage of the titanium enolate radical cations can be excluded for steric reasons. Equally, an alternative mechanism involving dissociative electron transfer can be definitely ruled out because reversible waves in the cyclic voltammograms as well as EPR spectra of the radical cations could be observed for all three compounds **1**–**3**. Hence, the mechanistic results indicate that the Ti–O bond of the radical cations $\mathbf{1}^{+\bullet}$–$\mathbf{3}^{+\bullet}$ is cleaved in a mesolytic bond dissociation process[19].

Two distinct alternatives for the mesolytic bond cleavage are possible: it can take place either by a homolytic or a heterolytic pathway[19]. The heterolytic variant has been observed in the deprotonation of enol radical cations as well as in the cleavage of silyl enol ether[22], enol phosphite[23], and enol phosphinate radical cations[23]. In contrast, homolytic cleavage was observed in enol ester[20], enol carbonate and enol carbamate radical cations[21].

Scheme 5. Modes of mesolytic bond cleavage



Homolytic bond scission of titanium enolate radical cations would lead to α-carbonyl cations and a titanium(III) species (Mech. B), while heterolytic cleavage would furnish α-carbonyl radicals and titanocene(IV) cations (Mech. A) (Scheme 6). α-Carbonyl radicals, however, are expected to undergo immediate oxidation to α-carbonyl cations under the applied conditions due to their low oxidation potentials [E_{pa}(**R1**) = +0.36 V, E_{pa}(**R2**) = +0.15 V and E_{pa}(**R3**) = +0.24 V][16c]. Regardless of which cleavage mode takes place, two equivalents of the appropriate one-electron oxidant are thus required in preparative reactions, because both the $Ti^{III}Cp_2Cl$ fragment (E_{pa} = −0.68 V)[24] and the α-carbonyl radicals **R1**–**R3** are easier to oxidize than the neutral titanium enolates. A distinction between the two mechanistic pathways due to the required amounts of oxidant is hence impossible.

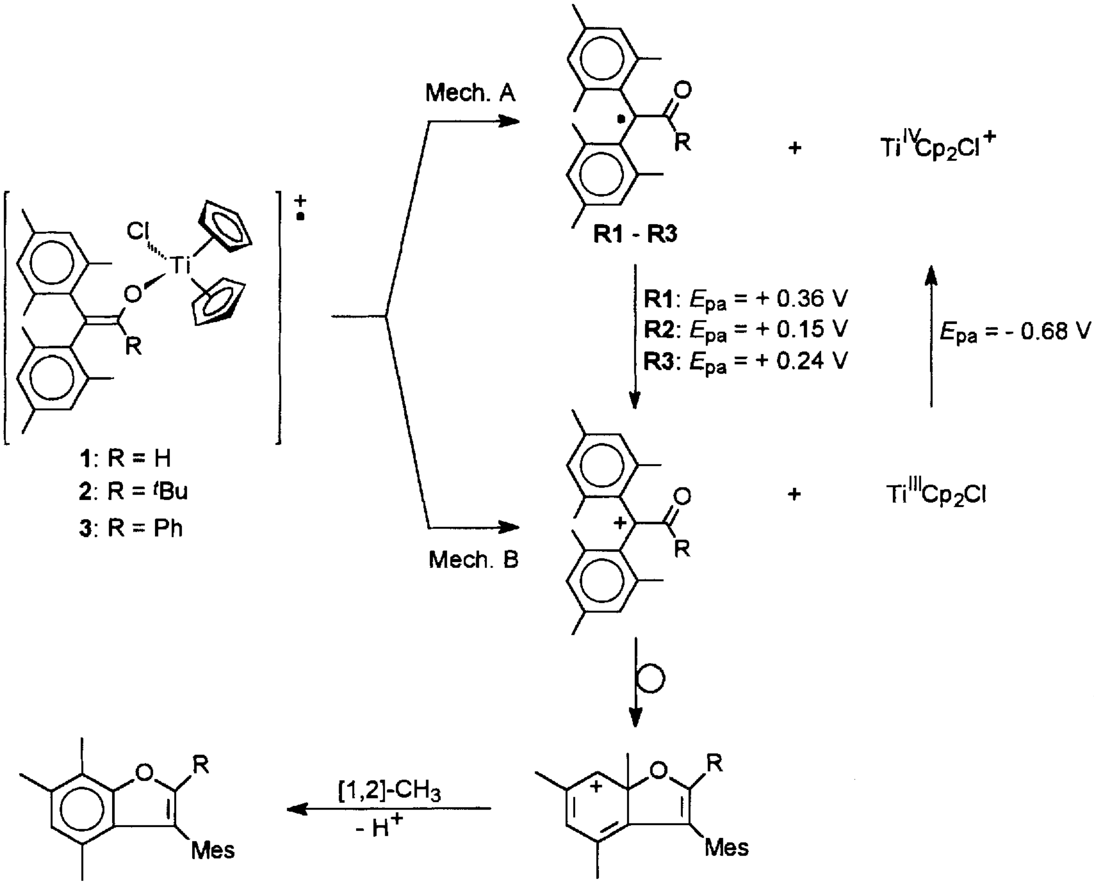
Simple thermochemical cycle calculations suggest bond cleavage of the titanium enolate radical cations $\mathbf{1}^{+\bullet}$–$\mathbf{3}^{+\bullet}$ to the α-carbonyl radicals (Mech. A), because the oxidation potential of $Ti^{III}Cp_2Cl$ is much lower than those of **R1**–**R3** (vide supra), resulting in a preference of Mech. A over Mech. B by 11–14 kcal mol^{-1} in acetonitrile (Scheme 7).

Kinetics of the Mesolytic Bond Cleavage

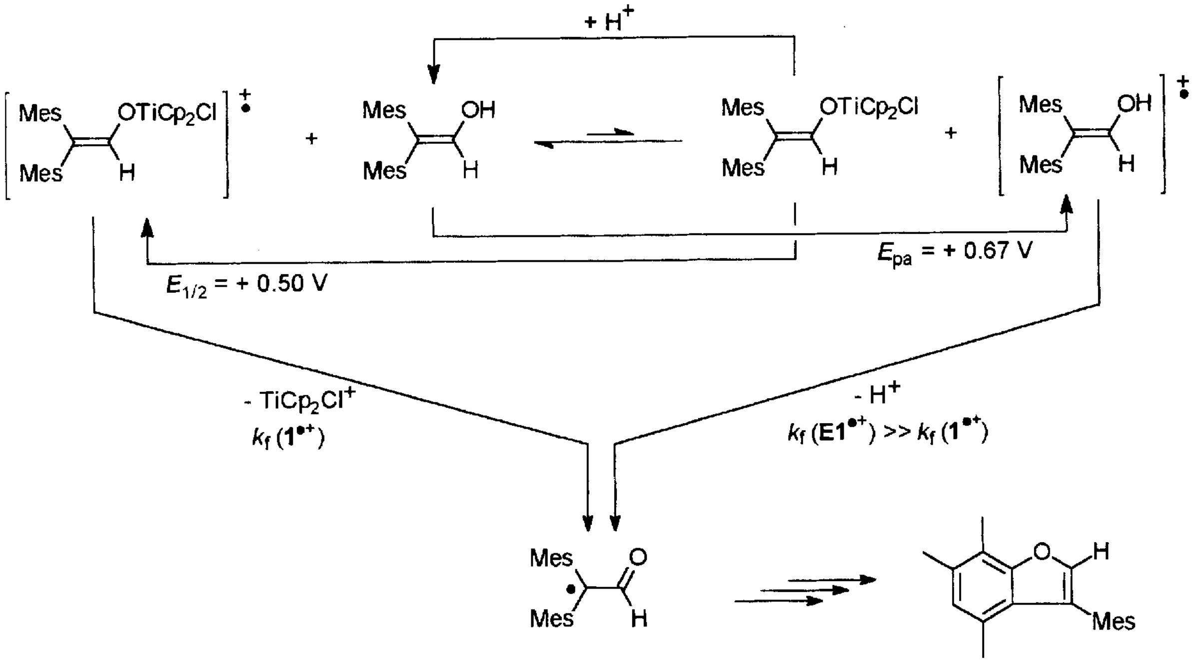
The kinetics of the mesolytic Ti–O bond cleavage in $\mathbf{1}^{+\bullet}$ was determined from the ratio of the peak currents I_{pc}/I_{pa} in CV measurements. For a precise kinetic analysis the mechanism of the follow-up reaction must be known and an appropriate working curve for this mechanism has to be calculated. However, in absence of base the mechanism is quite complex. As in the course of benzofuran formation protons are split off, the protolytic cleavage of neutral **1** to the corresponding enol **E1** takes place already on the time scale of the CV experiment. Thus, an additional reaction pathway for $\mathbf{1}^{+\bullet}$, that is intermolecular electron transfer from $\mathbf{1}^{+\bullet}$ to neutral enol **E1**, complicates the kinetic analysis. Although the electron transfer equilibrium, as determined by the potentials of the involved redox couples $\mathbf{1}/\mathbf{1}^{+\bullet}$ ($E_{1/2}$ = +0.50 V) and $\mathbf{E1}/\mathbf{E1}^{+\bullet}$ (E_{pa} = +0.67 V), is endergonic, the electron transfer from **E1** to $\mathbf{1}^{+\bullet}$ is a competitive reaction pathway to the mesolytic Ti–O bond cleavage, because $\mathbf{E1}^{+\bullet}$ is known to be very short-lived because of fast deprotonation ($k_f > 10^5$ s^{-1} in dichloromethane)[25].

Indeed, this mechanism could be corroborated by digital simulation of the cyclic voltammograms as they agreed well with those obtained from the electrochemical experiments. However, this complex mechanism does not allow for a rigorous kinetic interpretation of the partially reversible cyclic voltammograms of **1** in pure acetonitrile.

Scheme 6. Mechanism of benzofuran formation from titanium enolate radical cations



Scheme 7. Mechanistic situation after one-electron oxidation of **1**



Therefore we investigated the kinetics of the mesolytic Ti−O bond cleavage of **1** in acetonitrile in the presence of 20 equivalents of base to suppress the protolytic cleavage of neutral titanium enolate completely (see Figure 2). Now, the situation was simplified to an $EC_{irr}E$ mechanism and the kinetic analysis of the fragmentation was easily possible providing a first-order rate constant of the mesolytic Ti−O bond cleavage $k_f(\mathbf{1}^{+\bullet}) = 850 \pm 50\ s^{-1}$ at room temperature. This rate constant is similar to that of the $O-SiMe_2tBu$ bond cleavage in the corresponding silyl enol ether radical cation ($k_f = 1300\ s^{-1}$)[22]. Notably, $O-SiMe_2tBu$ silyl enol ethers have already been used successfully in oxidative C−C couplings[10].

EPR Investigations

By means of EPR spectroscopy we characterized for the first time titanium enolate radical cations in solution. The sterically congested species $\mathbf{1}^{+\bullet}$ and $\mathbf{3}^{+\bullet}$ show no hyperfine splitting in analogy to known radical cations of structurally related enol carbonates[21], enol carbamates[21] and enol phosphates[23]. For $\mathbf{4}^{+\bullet}$, however, a resolved EPR spectrum could be recorded. Digital simulation is in good agreement with the spectrum obtained from the EPR experiment, indicating that spin density is located on the enolato moiety. Although the mesityl is more electron rich than the phenyl group, spin density is higher on the phenyl moiety. AM1[26] calculations on the corresponding methyl enol ether radical cation illustrate, that the phenyl ring is twisted only about 15° out of plane of the double bond whereas the dihedral angle between the mesityl group and the double bond is approximately 55°. Accordingly, larger coupling constants a^H are plausible for the phenyl system. The corresponding methyl enol ether radical cation may be seen as an appropriate model for $\mathbf{4}^{+\bullet}$ because basically no spin density resides on the titanocene moiety and the steric demand of the titanocene fragment has almost no influence on the geometry of the aryl rings in β-position[14]. Since no spin density resides on the titanocene fragment EPR spectroscopy qualifies titanium enolate radical cations as electrophilic radicals which most likely react with nucleophiles at the β-carbon.

Nucleophilic Attack onto Titanium Enolate Radical Cations

Due to the extreme shielding of the β-carbon in the titanium enolates **1**−**3**, nucleophilic reactions at the β-carbon are excluded and thus the only observed primary reaction of their radical cations is the mesolytic bond cleavage followed by benzofuran formation. Interestingly, the sterically less shielded $\mathbf{4}^{+\bullet}$ allows for reaction with nucleophiles as shown by the formation of the oxazole derivative **O4**. Oxazole formation can be explained either by the nucleophilic attack of acetonitrile onto $\mathbf{4}^{+\bullet}$ or onto the α-carbonyl cation after mesolytic cleavage. Since acetonitrile is a rather poor nucleophile whose attack onto the corresponding methyl enol ether radical cation is known to be fairly sluggish ($k_2 < 7\ M^{-1}\ s^{-1}$, resulting in a pseudo-first order rate constant $k < 10^2\ s^{-1}$)[16b] as compared to Ti−O bond cleavage ($k = 850\ s^{-1}$ for $\mathbf{1}^{+\bullet}$), we rather assume that attack at the stage of the α-carbonyl cation has taken place.

After reaction with one equivalent of oxidant the sterically uncongested titanium enolate **6** furnished the dimerization product **D6**, indicative of the fact that C−C bond formation must have taken place at some stage (Scheme 4). While the mechanism of this reaction is not known yet, we assume from the fast rate constants of unhindered olefin radical cations with olefins[27] that $\mathbf{6}^{+\bullet}$ is reacting with neutral **6** or $\mathbf{6}^{+\bullet}$ prior to Ti−O bond cleavage. Indeed, thermochemical cycle calculations show, that the free energy for the mesolytic bond cleavage in $\mathbf{1}^{+\bullet}$ and $\mathbf{6}^{+\bullet}$ differ by less than 2 kcal mol^{-1}, as a consequence of the small difference in the oxidation potentials of the titanium enolates. One now can deduce that the kinetics of this scission should not differ vastly. However, **1** already shows signs of reversible oxidation at scan rates $\geqslant 20\ V\ s^{-1}$ whereas no reduction wave for **6** could be monitored even at scan rates up to $40000\ V\ s^{-1}$ (both experiments performed in dichloromethane). This suggests, that in $\mathbf{6}^{+\bullet}$ an alternative follow-up reaction takes place which is at least about the factor $2 \cdot 10^3$ faster than bond cleavage. This follow-up reaction is expected to be the C−C bond formation between $\mathbf{6}^{+\bullet}$ and either neutral **6** or the radical cation $\mathbf{6}^{+\bullet}$.

In summary, we characterized titanium enolate radical cations in solution for the first time by CV and EPR spectroscopy. The sterically congested representatives **1**−**3** undergo a clean Ti−O bond cleavage according to Mech. A into α-carbonyl radicals and cationic titanocene(IV) species. Since this mesolytic bond scission is slow, sterically unhindered titanium enolates can undergo direct carbon−carbon bond formation processes with π-nucleophiles on the stage of their radical cations.

We gratefully acknowledge the financial support by the *Deutsche Forschungsgemeinschaft* (SFB 347: "Selective Reactions of Metal Activated Molecules"). In addition, we are most indebted to the *Fonds der Chemischen Industrie* for the ongoing support of our research. We thank the *Degussa* for a generous gift of electrode materials and furthermore Dr. *G. Gescheidt*, Basel for helpful discussions.

Experimental Section

^1H and ^{13}C NMR: Bruker AM 200 (200 MHz) and AM 250 (250 MHz), int. TMS. − Supporting electrolyte tetra(*n*-butyl)ammonium hexafluorophosphate (Fluka) was of electrochemical grade and used without further purification. − Solvents for CV measurements, EPR spectroscopy and one-electron oxidation experiments: acetonitrile was purchased in HPLC quality from Riedel-de-Haën, distilled from calcium hydride and filtered through basic alumina (ICN); dichloromethane was purchased in HPLC quality from Merck, distilled from P_4O_{10} and filtered through basic alumina (ICN). − The titanium enolates **1**−**5** were prepared as described in ref.[14] and **6** as reported in ref.[9a]

General Procedure for One-Electron Oxidations: In an argon filled glovebox the desired amounts of the one-electron oxidant $Fe(phen)_3(PF_6)_3$ and the titanium enolates were placed into two separate test tubes equipped with stirring rods. At a high purity argon line, 3 ml of the appropriate solvent (acetonitrile or dichloromethane) was added in each test tube to dissolve the reactants. When the blue solution of the one-electron oxidant was added through a syringe to the solution of the titanium enolate, the color of the mixture turned immediately to a bright red. The resulting mixture was stirred for 1 min, quenched with 10 ml of saturated aqueous $NaHCO_3$ and diluted with 10 ml of dichloromethane. The aqueous layer was extracted three times with CH_2Cl_2 and the combined organic layers were washed with water and dried with

Na_2SO_4. The solution was filtered through silica gel in order to remove the red $Fe(phen)_3(PF_6)_2$ as well as titanium fragments split off in the course of the reaction. Removal of the solvent afforded the crude product. Product analysis was performed by ^{1}H NMR spectroscopy. All products were identified by comparison with data of authentic samples. For 3-mesityl-4,6,7-trimethylbenzofuran (**B1**) see ref.[16a], for 2-*tert*-butyl-3-mesityl-4,6,7-trimethylbenzofuran (**B2**) see ref.[16a], for 3-mesityl-2-phenyl-4,6,7-trimethylbenzofuran (**B3**) see ref.[16d], for 4-mesityl-2-methyl-5-phenyloxazole (**O4**) see ref.[16b] and for 2,3-dimethyl-1,4-diphenylbuta-1,4-dione (**D6**) see ref.[28]. The yields were determined by adding *m*-nitroacetophenone as an internal ^{1}H-NMR standard.

Cyclic Voltammetry: In a glove box tetra(*n*-butyl)ammonium hexafluorophosphate (232 mg, 600 μmol) and the electroactive species (6 μmol) were placed into a thoroughly dried CV cell. At a high purity argon line acetonitrile or dichlormethane (6.0 ml) was added through a gastight syringe. Then a platinum disc working electrode (∅ = 1 mm), a platinum wire counter electrode and a silver wire as pseudo reference electrode were placed into the solution. The cyclic voltammograms were recorded at various scan rates using different starting and switching potentials. For determination of the oxidation potentials, ferrocene ($E_{1/2}$ = +0.39 V vs. SCE) was added as the interal standard. Cyclic voltammograms were recorded using a Princeton Applied Research Model 362 potentiostat with a Philips model PM 8271 *X, Y,t*-recorder for scan rates < 1 V s^{-1}. For fast scan cyclic voltammetry, a Hewlett Packard model 3314A function generator was used connected to a three-electrode potentiostat developed by C. Amatore[29]. The employed working electrodes were self-made gold (diameter: 25 μm) and platinum (diameter: 10 μm) ultramicroelectrodes. The ratios I_{pc}/I_{pa} were determined according to the procedure of Nicholson[30].

EPR Spectroscopy: Titanium enolate radical cations were generated by oxidation of the neutral precursor (6 μmol) with the one-electron oxidant tris(*p*-bromophenyl)aminium hexafluoroantimonate (5 μmol) in dichloromethane (2 ml) using high vacuum techniques in sealcs glass tubes at −100°C. Due to the intensive red color of neutral titanium enolates in solution no significant change in color could be observed in the course of one-electron oxidations. The samples were kept at this temperature as short as possible in order to avoid decomposition. EPR spectra were recorded on a Bruker ESP300 spectrometer at −100°C. Digital simulations of the EPR spectra were performed using PEST simulation freeware from the National Institute of Environmental Health Sciences.

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[1] Part 5: See ref.[21].

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