

Kinetics and mechanism of thioether oxidation with H_2O_2 in the presence of Ti(IV)-substituted heteropolytungstates

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Abstract

Kinetics of thioether oxidation with concentrated (86%) and diluted (35%) aqueous H_2O_2 in the presence of catalytic amounts of $(\text{Bu}_4\text{N})_7\{[\text{PW}_{11}\text{O}_{39}\text{Ti}]_2\text{OH}\}$ dimeric heteropolytungstate (**1**) has been studied in acetonitrile. With 86% H_2O_2 the reaction was found to be first order in the oxidant, 0.5 order in the catalyst and practically independent on the sulfide concentration and its nature, whereas with 35% H_2O_2 the reaction was first order in both the catalyst and substrate, the order in the oxidant being changed from first to zero with increasing H_2O_2 concentration. Both ^{31}P NMR and kinetic data are consistent with mechanism, including fast dissociation of **1** to the monomer (**2**), the equilibrium formation of active hydroperoxo complex $\text{PW}_{11}\text{TiOOH}$ (**B**) from **2**, and interaction of **B** with thioether. The rate-limiting steps are the formation of **B** and the interaction of **B** with sulfide at low and high H_2O concentrations, respectively. The kinetic study of stoichiometric reaction between **B**, generated in situ from inactive side-on peroxo complex $\text{PW}_{11}\text{TiO}_2$ (**A**), and thioethers showed first order dependence on both **B** and sulfide concentration, thus indicating that no binding of thioether to Ti(IV) occurs. The lack of Hammett-type correlation and specific products obtained in oxidation of benzyl phenyl sulfide allowed to rule out electrophilic oxygen transfer and suggest a mechanism that involves the formation of a thioether cation radical intermediate. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Titanium-substituted heteropolytungstates; Hydrogen peroxide; Thioether oxidation; Kinetics; Mechanism

1. Introduction

Transition-metal-substituted heteropolyanions (HPAs) due to the exclusively inorganic nature of their coordination sphere can combine the selectivity advantages of homogeneous catalysts with stability advantages of heterogeneous catalysts ([1] and references cited therein). Further-

more, they can be used as homogeneous models for studying the mechanisms of the catalytic action of heterogeneous catalysts in oxidation reactions. Recently, we have found that Keggin-type Ti(IV)-monosubstituted HPAs, $\text{PW}_{11}\text{Ti}(\text{L})\text{O}_{39}^{n-}$ ($\text{PW}_{11}\text{Ti}(\text{L})$ for short), show pronounced catalytic activity in thioether oxidation with H_2O_2 [2–4]. The preparation and characterization of the new dimeric heteropolytungstate $(\text{Bu}_4\text{N})_7\{[\text{PW}_{11}\text{O}_{39}\text{Ti}]_2\text{OH}\}$ (**1**) have been reported [4]. Dimer **1** was found to form from the well-known monomer PW_{11}TiO upon acidification, the protonated monomer PW_{11} -

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TiOH (**2**) being the key intermediate in the dimerization process. Both dimer **1** and monomer **2** react with H_2O_2 to yield hydroperoxo complex $\text{PW}_{11}\text{TiOOH}$ (**B**), which has been proved to oxidize thioethers under stoichiometric conditions [4]. Here, we report kinetic studies of both catalytic thioether oxidation with H_2O_2 in the presence of **1** and stoichiometric reaction of **B** with thioethers. These studies together with ^{31}P NMR data allowed to get further insight into the mechanism of the title reaction.

2. Experimental

2.1. Materials

Acetonitrile (Fluka, HPLC grade) was dried and stored over activated 4A molecular sieves. Methyl phenyl sulfide (MPS), methyl *p*-tolyl sulfide (MTS), methyl *p*-methoxyphenyl sulfide (MMPS), *p*-bromophenyl methyl sulfide (Br-PMS), *p*-nitrophenyl methyl sulfide (NO_2 -PMS) and benzyl phenyl sulfide (BPS) were purchased from Fluka. MPS, MTS, BPS and MMPS were used as received, the other thioethers were purified by recrystallization from MeOH. Triflic acid (TfOH, Merk) was used as 0.2 M solution in MeCN and titrated prior to use. Hydrogen peroxide (35%) was concentrated in vacuum up to 86% and determined by iodometric titration just before use. All other chemicals were the best available reagent grade. The dimeric heteropolytungstate $(\text{Bu}_4\text{N})_7\{[\text{PW}_{11}\text{O}_{39}\text{Ti}]_2\text{OH}\}$ (**1**) and the peroxo complex $(\text{Bu}_4\text{N})_5\text{PW}_{11}\text{TiO}_{41}$ (**A**) were prepared as described in Ref. [4]. The active hydroperoxo complex ($\text{PW}_{11}\text{TiOOH}$, **B**) was generated in situ by the addition of 1 equiv. TfOH to a solution of **A** just before the experiments.

2.2. Kinetic measurements

Kinetic experiments for catalytic oxidation were performed in a thermostated ($\pm 0.2^\circ\text{C}$)

glass reactor equipped with a magnetic stirrer, a reflux condenser and Ar supplier. The reaction was initiated by injection of the oxidant (0.02–0.2 M) to MeCN solution (5 ml) containing an organic sulfide (0.1–2.0 M) and **1** (0.00025–0.005 M). For diluted H_2O_2 , the dependence of the reaction rate on $[\text{H}_2\text{O}_2]$ was studied at fixed water concentration (0.7 M) in order to standardize the reaction conditions. Aliquots were taken from the reaction mixture by 1000 μl syringe, and H_2O_2 consumption was determined by iodometric titration. The initial-rate method and \ln – \ln plots were employed to determine the reaction orders. Duplicate runs usually agreed within 7–10%. The stoichiometric reaction was performed in a thermostated quartz cell ($l = 1.0$ cm). One equivalent of TfOH was added to a MeCN solution of peroxo complex **A** (0.0005 M) to generate hydroperoxo complex **B**, and then the reaction was started by the addition of thioether substrate (0.05–0.5 M). The time course of the reaction was observed by monitoring the disappearance of **B** ($\lambda_{\text{max}} = 410$ nm and $\varepsilon = 2000$ $\text{M}^{-1} \text{cm}^{-1}$ in MeCN). The rate constant was evaluated using the integrated first-order rate law under pseudo-first-order conditions.

2.3. Instrumentation

GC-MS spectra of BPS oxidation products were run using an LKB-2091 instrument. ^{31}P NMR spectra were recorded at 161.98 MHz on an MSL-400 Bruker spectrometer. Chemical shifts, δ , were referenced to 85% H_3PO_4 . Electronic absorption spectra were run on a Shimadzu UV-300 spectrophotometer.

3. Results and discussion

Previously, we have found that the rate of the catalytic thioether oxidation with H_2O_2 in the presence of **1** increased with increasing H_2O concentration in MeCN [4]. We suggested that this was probably caused by dissociation of **1**,

producing monomer **2**, which reacts more rapidly with H₂O₂ as compared to **1** to yield active hydroperoxo complex **B**. The dimer/monomer ratios at different H₂O concentrations together with initial rates of the formation of **B**, estimated from ³¹P NMR data, are given in Table 1. The slight upfield shift of ³¹P NMR signal of **2** is due to the change in solution magnetic susceptibility with increasing water content in MeCN, while a large upfield shift of the signal of **1** results from deprotonation of the Ti–O(H)–Ti bridge in the presence of H₂O yielding Ti–O–Ti species, which are in fast on the ³¹P NMR time scale proton exchange with the Ti–O(H)–Ti species [4]. The dissociation equilibrium is fast. Rough evaluation of the dimer dissociation constant gave the value $K_{\text{dis}} \sim 10^{-3}$. Upon addition of H₂O₂, the signal of **2** disappeared first, and the signal of PW₁₁TiOOH appeared simultaneously. The disappearance of **1** is much slower than the disappearance of **2** (Fig. 1).

The kinetic studies were performed with both diluted (35%) and concentrated (86%) H₂O₂ using MPS as a model substrate and dry MeCN as a solvent. Typical kinetic curves showed no induction period, autocatalysis or inhibition behavior. The absence of any effect of light, oxygen or added chain radical scavengers, such as hydroquinone, on the reaction rate allowed to rule out chain radical mechanism. Interestingly,

different experimental rate laws have been found for concentrated and diluted H₂O₂. With 86% H₂O₂, the reaction was first order in the oxidant (Fig. 2) and 0.5 order in the catalyst (Fig. 3A). The rate was slightly dependent on the sulfide concentration (Fig. 3B) and practically independent on the sulfide nature ($V_0 = 3.0 \pm 0.3$ and $2.9 \pm 0.2 \text{ M c}^{-1}$ for oxidation of MPS and MTS, respectively). At the same time, the reaction with 35% H₂O₂ appeared to be first order in the catalyst (Fig. 4A) and substrate (Fig. 4B), the order in the oxidant being changed from first to zero with increasing H₂O₂ concentration (Fig. 5). Earlier, the oxidation of thioethers with *t*-butyl hydroperoxide in the presence of TiO(acac)₂ and Ti(OPrⁱ)₄ has been found to be first order in the catalyst and oxidant and fractional positive order in substrate, which was explained by coordination of the sulfides to Ti(IV) [5]. However, ³¹P NMR, which has been shown to be very sensitive to the changes in HPA coordination sphere, revealed no change in the chemical shift or width of the signal of **1** upon addition of the sulfide [3,4]. Moreover, first-order dependencies on both the oxidant and substrate concentrations have been found for the rate of the stoichiometric thioether oxidation with generated in situ hydroperoxo complex **B** (Figs. 6 and 7, respectively). All these data collectively show that no binding of thioether to Ti(IV)-HPA or **B** occurs. Slight dependence on the substrate concentration may indicate that the substrate is not involved in the slow step of the catalytic reaction. All the data are most consistent with the mechanism, including fast dissociation of **1** to monomer **2** (Eq. 1), the equilibrium formation of active hydroperoxo complex **B** from **2** (Eq. 2), and interaction of **B** with thioether (Eq. 3):

Table 1

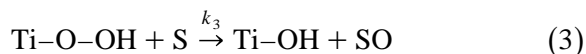
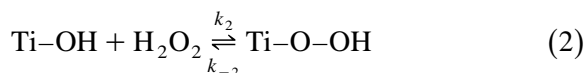
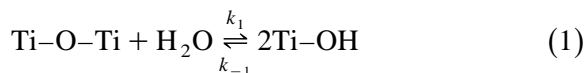
The relationship between H₂O content in MeCN, the dimer (**1**)/monomer (**2**) molar ratio and the initial rate of hydroperoxo complex **B** formation

H ₂ O (% v/v)	[1] ^a × 10 ³ (M) (δ ^b)	[2] × 10 ³ (M) (δ ^b)	V ₀ ^c × 10 ⁶ (M c ⁻¹)
0	2.5 (12.76)	–	0.071
1	2.4 (12.80)	0.2 (13.39)	0.47
3	2.2 (12.98)	0.6 (13.50)	1.8
10	1.4 (13.45)	2.2 (13.59)	6.4

^aTotal concentration of the protonated (Ti–O(H)–O) and unprotonated (Ti–O–Ti) dimeric forms.

^b³¹P NMR chemical shift (ppm).

^cInitial rate of the hydroperoxo complex formation at 20°C, estimated from ³¹P NMR data.



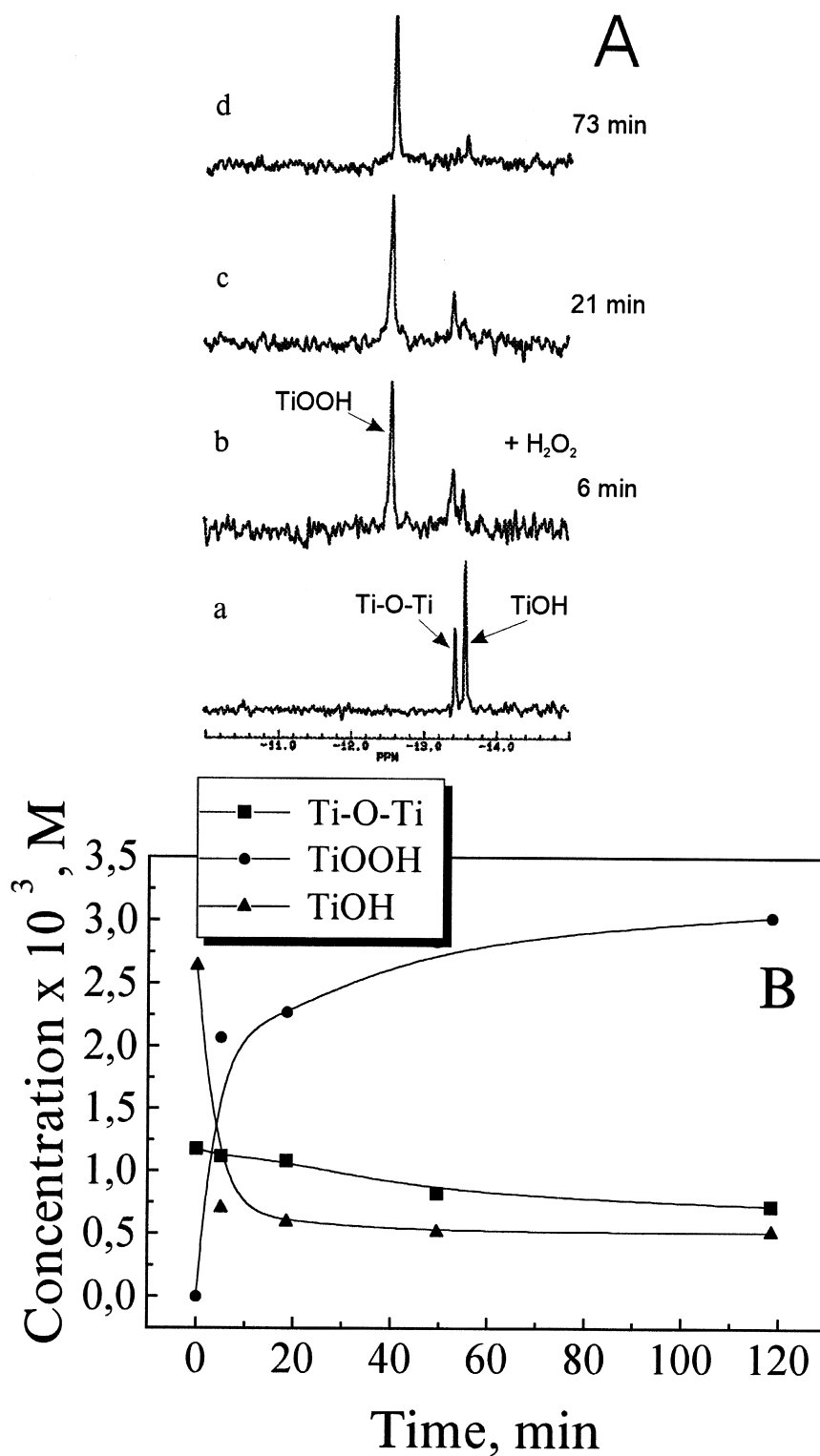


Fig. 1. (A) ^{31}P NMR spectra of **1** in MeCN–H₂O before (a) and after addition of H₂O₂ (b–d) and (B) the corresponding time dependence of [**1**], [**2**] and [PW₁₁TiOOH] ([**1**]₀ = 2.5×10^{-3} M, (H₂O₂) = 0.1 M, 10% v/v H₂O, 20°C).

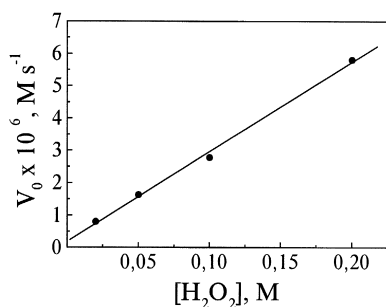


Fig. 2. Plot of the initial rate (V_0) of MPS oxidation by 86% H_2O_2 in the presence of **1** versus $[\text{H}_2\text{O}_2]$. $[\text{I}] = 2.5 \times 10^{-4} \text{ M}$, $[\text{MPS}] = 0.5 \text{ M}$, 25°C .

Different rate laws, found experimentally for diluted and concentrated H_2O_2 , may be rationalized by assuming that rate-limiting steps are different for low and high H_2O concentrations. Indeed, at low $[\text{H}_2\text{O}]$ (0.0226 M when used 86% H_2O_2), the equilibrium (Eq. 1) is shifted left and the formation of TiOOH (Eq. 2) may be rate-limiting. This assumption leads to the rate law $V_0 = k_2 K_1^{0.5} [\text{Ti-O-Ti}]^{0.5} [\text{H}_2\text{O}_2] [\text{S}]^0$, where $K_1 = k_1 [\text{H}_2\text{O}] / k_{-1}$, which agreed with the rate law obtained experimentally. On the contrary, when diluted H_2O_2 was used ($[\text{H}_2\text{O}] = 0.7 \text{ M}$),

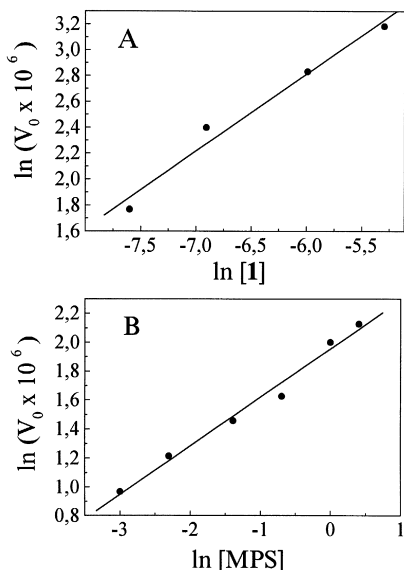


Fig. 3. (A) Plot of $\ln V_0$ versus $\ln [\text{I}]$ ($[\text{H}_2\text{O}_2] = 0.1 \text{ M}$, $[\text{MPS}] = 0.5 \text{ M}$, 25°C) and (B) plot of $\ln V_0$ versus $\ln [\text{MPS}]$ ($[\text{H}_2\text{O}_2] = 0.1 \text{ M}$, $[\text{I}] = 1 \times 10^{-3} \text{ M}$, 25°C) for MPS oxidation with 86% H_2O_2 .

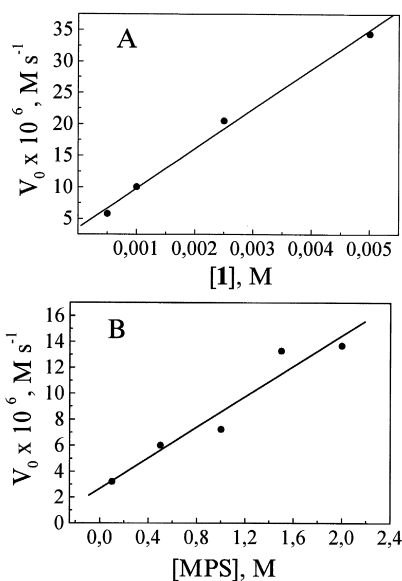


Fig. 4. (A) Plot of the initial rate (V_0) versus $[\text{I}]$ ($[\text{H}_2\text{O}_2] = 0.1 \text{ M}$, $[\text{MPS}] = 0.5 \text{ M}$, 25°C) and (B) plot of V_0 versus $[\text{MPS}]$ ($[\text{H}_2\text{O}_2] = 0.1 \text{ M}$, $[\text{I}] = 5 \times 10^{-4} \text{ M}$, 25°C) for MPS oxidation by 35% H_2O_2 in the presence of **1**.

the equilibrium (Eq. 1) is shifted right (this is in accordance with ^{31}P NMR data), the rate of

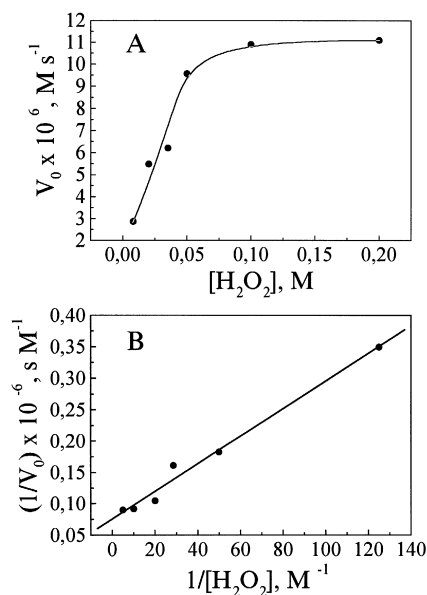


Fig. 5. (A) Plot of the initial rate (V_0) versus $[\text{H}_2\text{O}_2]$ and (B) plot of $1/V_0$ versus $1/[\text{H}_2\text{O}_2]$ for MPS oxidation by 35% aqueous H_2O_2 in the presence of **1**. $[\text{I}] = 5 \times 10^{-4} \text{ M}$, $[\text{MPS}] = 0.5 \text{ M}$, $[\text{H}_2\text{O}] = 0.7 \text{ M}$, 25°C .

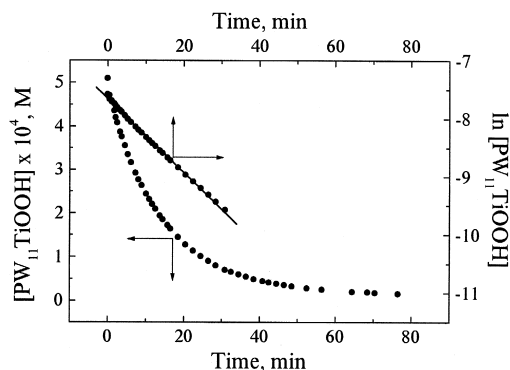


Fig. 6. Time dependence of $[PW_{11}TiOOH]$ for stoichiometric oxidation of MPS (0.05 M) at 25°C and the corresponding plot of $\ln[PW_{11}TiOOH]$ versus time.

the peroxo complex formation enhances, and the interaction of **B** with sulfide becomes rate-limiting. The derived rate law, expressed in terms of total catalyst, is $V_0 = k_3 K_2 [S][Ti-O-Ti]_0 [H_2O_2] / (1 + K_2 [H_2O_2])$, where $K_2 = k_2 / k_{-2}$. The order with respect to H_2O_2 would then be expected to vary from first- to zero order as a function of H_2O_2 concentration, which is consistent with the experimental data. K_2 and k_3 estimated from the plot of $1/V_0$ versus $1/[H_2O_2]$ were found to be $35 \pm 2 M^{-1}$ and $0.053 \pm 0.006 M^{-1} s^{-1}$, respectively. Note that a similar value of K_2 ($40 \pm 4 M^{-1}$) was estimated independently from ^{31}P NMR and UV-Vis studies of equilibrium (Eq. 2). Earlier $TiO(acac)_2$ -catalyzed thioether oxidation with H_2O_2 was found to be zero order in the oxidant, which was interpreted as arising from a large value of the association constant H_2O_2 -Ti(IV) [6].

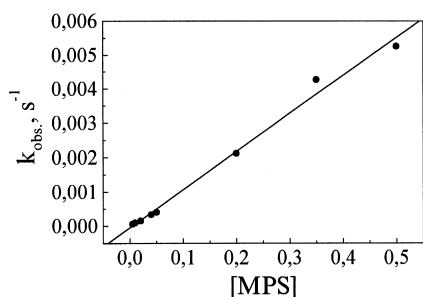


Fig. 7. Plot of pseudo-first-order constant k_{obs} versus $[MPS]$ for stoichiometric oxidation of MPS by $PW_{11}TiOOH$ ($5 \times 10^{-4} M$) at 25°C.

In order to have more details about the mechanism of the interaction of hydroperoxo complex **B** with thioether, we have studied the kinetics of step (Eq. 3) independently. **B** was generated in situ by the addition of 1 equiv. of protons to stable peroxo complex **A**. Again, **B** was found to decay by a first-order process $\ln[B] = -k_{obs}\tau + \text{const}$ up to 70–80% conversion (Fig. 6). The linear dependence of the pseudo-first-order constant k_{obs} on the substrate concentration over a wide range of $[S]$ ($[B] = 0.0005 M$, $[S] = 0.005$ – $0.5 M$) indicates that no strong binding between the sulfide and **B** occurs (Fig. 7). The stoichiometric oxidations of *p*-substituted phenyl methyl sulfides with **B** revealed a lack of Hammett free-energy correlation between second-order rate constant k and σ values (Table 2). Note that the values of k obtained for stoichiometric oxidation are of the same order of magnitude as the values of k_3 estimated for the catalytic reaction. However, this comparison should be made with some caution, in view of the differences in the reaction conditions (H_2O concentration, acidity, the presence of triflate anions, etc.).

The oxidation of a test substrate, BPS, under both turnover and stoichiometric conditions was found to yield benzaldehyde along with the corresponding sulfoxide and sulfone. Benzaldehyde is known to be a typical product of BPS radical cation fragmentation [7]. Thus, we may conclude that the mechanism of the Ti(IV)-HPA-catalyzed thioether oxidation with H_2O_2 is in sharp contrast to the conventional mechanism via electrophilic oxygen transfer estab-

Table 2

Rate constants of the stoichiometric oxidation of methyl *p*-X-phenyl sulfides by generated in situ $PW_{11}TiOOH$ hydroperoxo complex

Substituent X	Hammett constant σ	$k \times 10^2 (M^{-1} s^{-1})$
CH_3O	-0.27	5.9
CH_3	-0.17	2.8
-	0	1.4
Br	0.23	5.3
NO_2	0.78	2.0

lished for d₀-transition-metal-mediated peroxide oxidations [8–12] and involves the formation of thioether radical cation.

4. Conclusions

The mechanism of thioether oxidation with H₂O₂ in the presence of Ti(IV)-HPA dimer **1** includes fast dissociation of **1** to the monomer form **2**, the equilibrium formation of active hydroperoxo complex **B** from **2**, followed by its interaction with thioether. The rate-limiting steps are the formation of **B** and the reaction between **B** and sulfide at low and high H₂O concentrations, respectively. The interaction of **B** with organic sulfides proceeds via the formation of thioether cation radical.

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