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Homogeneous Catalysis of *n*-Propyl Mercaptan Oxidation with a Cobalt Tetraphenylporphyrin Complex

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Abstract—A kinetic study of the oxidation of *n*-propyl mercaptan (PrSH) with chloridotetraphenylporphyrinatocobalt(III) in the absence of oxygen has been performed. The activation parameters of this reaction have been found to be close to those of the oxidation step of the Co(II) complex, and the structure of the transition state has been hypothesized. A stepwise mechanism of PrSH oxidation in the presence of Co complexes is proposed, comprising the sequential oxidation of PrSH with cobalt(III) tetraphenylporphyrinate and the oxidation of the resulting Co(II) complex with oxygen. The adequacy of the proposed scheme has been kinetically substantiated using the experimental data.

Keywords: propyl mercaptan, oxidation, cobalt tetraphenylporphyrin complex

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Issues relating to the catalytic hydroprocessing of petroleum fractions seem to have been most exhaustively discussed in [1, 2], the problems of hydrogenolysis of polyaromatic sulfur compounds have been covered by Whitehurst et al. [3], and the specific features of hydrotreating have been surveyed by Vasudevan and Fierro [4]. Demercaptanization consists in the oxidation of thiols to disulfides in the presence of metal complex catalysts. The most efficient method of the treatment of hydrocarbons for the removal of mercaptans is their extraction with an aqueous alkali solution involving the oxidation of mercaptans with atmospheric oxygen in the presence of phthalocyanine complexes with transition metals as a catalyst [4]. Thus, mercaptans are oxidized to disulfides, which can be isolated in pure form.

Analysis of published data [5–8] shows that despite numerous studies in the past decades on the catalytic oxidation of organic sulfur compounds, the ideas on the mechanism of oxidation of mercaptans are still controversial. The lack of understanding hinders the creation of high-performance catalysts for desulfurization of hydrocarbons, which can help to solve a number of environmental and engineering problems. Reliable concepts of the mechanism of the process are needed for the development of advanced catalysts, as they ensure the optimal state of the reaction center of the catalyst system.

In this context, the present work in continuation of previous studies [9, 10] is devoted to investigation of the oxidation of *n*-propyl mercaptan (PrSH) with chloridotetraphenylporphyrinatocobalt(III) ($ClCo^{III}TPP$) in the absence of oxygen.

EXPERIMENTAL

Chloridotetraphenylporphyrinatocobalt(III) ($ClCo^{III}TPP$) was obtained by oxidation of cobalt(II) tetraphenylporphyrinate ($Co^{II}TPP$) with air oxygen (bubbling for 2 h) and addition of hydrochloric acid ($Co^{II}TPP : HCl \sim 1 : 1$). Co^{II} was synthesized according to the procedure described in [10]. The solvent was absolute ethanol 99.9%. The oxidation reaction of *n*-propyl mercaptan with chloridotetraphenylporphyrinatocobalt(III) in absolute ethanol was carried out by rapid mixing of deoxygenated PrSH and $ClCo^{III}TPP$ solutions.

Electronic absorption spectra of the solutions were recorded on a Perkin-Elmer UV–VIS Lambda 20 versatile spectrometer with a wavelength accuracy of ±0.1 nm. A Peltier temperature programmer was used for measurements at different temperatures. All the measurements were performed in standard quartz cells with an optical path length of 0.499 or 1 cm in the temperature range of 298.15–318.15 K.

Rate constants were calculated with the use of a program based on the generalized nonlinear least-squares method implemented with the help of the flexible polyhedron method [11]. The experiment involved measuring the absorbance using a spectrophotometer with automatic digital recording. Absorbance values measured over the entire range of wavelengths were input into the computation program, as

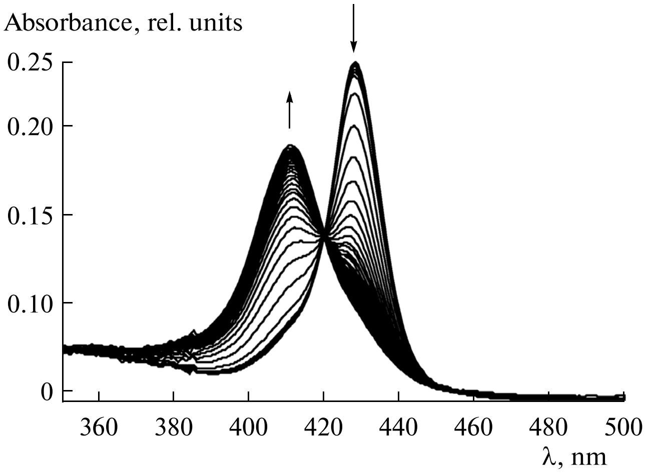


Fig. 1. Changes in electronic absorption spectrum during the oxidation of *n*-propyl mercaptan with chloridotetraphenylporphyrinatocobalt(III) at T = 298.15 K, $C(\mathrm{ClCo^{III}TPP}) = 8.11 \times 10^{-6}$ mol/L, and $C(\mathrm{C_3H_7SH}) = 3.70 \times 10^{-4}$ mol/L.

well as the time of recording the electronic absorption spectra. The error in the determination of the reaction rate constants did not exceed 5%. The values of the activation energy and the pre-exponential factor were determined from the ln $\ln k_v = f(1/T)$ plot, and the other activation parameters (enthalpy, free energy, and entropy) were found as specified in [12].

The equilibrium constant of the oxidation process (K_p) was calculated by the formula proposed in [13]:

$$K_p = \frac{A_\tau - A_o}{A_\infty - A_\tau}\,\frac{1}{C_l^0 - C_{\mathrm{MP}}^0 \dfrac{A_\tau - A_o}{A_\infty - A_\tau}},$$

where A_o, A_τ, A_∞ are the absorbances at the operating wavelength of metal complex solutions at times 0, τ, and on completion of the reaction, respectively; C_l^0 is the initial ligand concentration in mol/L; and C_{MP}^0 is the initial concentration of the metal complex, mol/L. The values of the thermodynamic quantities entropy and enthalpy were determined graphically from the ln $\ln K_p = f(1/T)$ plot.

RESULTS AND DISCUSSION

A typical example of spectral changes caused by addition of propyl mercaptan to $\mathrm{ClCo^{III}TPP}$ is shown in Fig. 1. The intensity of the bands due to $\mathrm{ClCo^{III}TPP}$ (427.4 nm) is continuously decreases, and the absorption band corresponding to the reduced form $\mathrm{Co^{II}TPP}$ increases. The single distinct isosbestic point indicates the formation of only one product.

To determine the reaction order in $\mathrm{ClCo^{III}TPP}$ and *n*-propyl mercaptan, a set of experiments was carried out at a constant porphyrin concentration and 298.15 K under anaerobic conditions in an absolute ethanol medium.

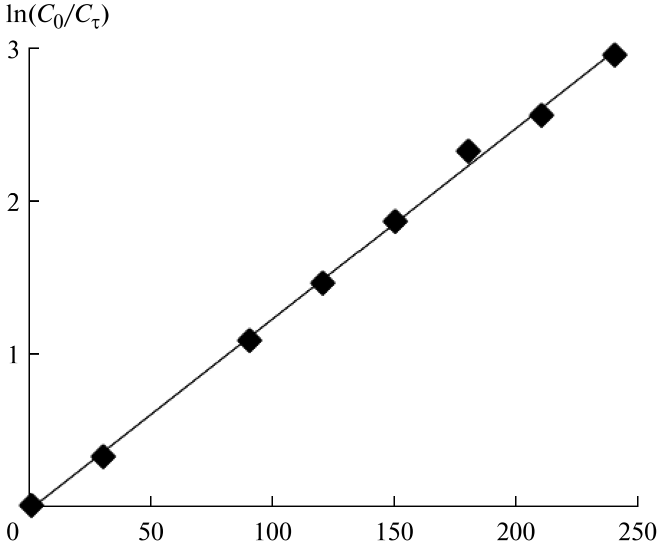


Fig. 2. Change in absorbance at 425 nm during the oxidation of *n*-propyl mercaptan with chloridotetraphenylporphyrinatocobalt(III) in ethanol at T = 298.15 K, $C(\mathrm{ClCo^{III}TPP}) = 8.11 \times 10^{-6}$ mol/L, and $C(\mathrm{C_3H_7SH}) = 2.47 \times 10^{-4}$ mol/L.

The linear relationship $\ln(C_0/C_\tau) = f(\tau)$ (where C_0 and C_τ are respectively the initial and current concentrations of $\mathrm{ClCo^{III}TPP}$) at 30-fold excess of PrSH relative to $\mathrm{ClCo^{III}TPP}$ (Fig. 2) suggests the first-order reaction in the complex.

Quantitative analysis of the absorption spectra (Fig. 1) made it possible to calculate the effective rate constants, which were used to determine the order of the reaction in mercaptan. The linear dependence of ln k_{eff} on $\ln C(\mathrm{C_3H_7SH})$ with a slope equal to unity (Fig. 3) shows the first order of the oxidation reaction with respect to the substrate. Thus, it can be stated that the oxidation of *n*-propyl mercaptan with cobalt(III) tetraphenylporphyrinate in the absence of oxygen occurs via the following scheme:

$$\begin{aligned}&\mathrm{ClCo^{III}TPP + C_3H_7SH}\\ &\longleftrightarrow \mathrm{Co^{II}TPP + Cl^- + C_3H_7S^{\bullet} + H^+}.\end{aligned} \qquad \text{(I)}$$

Scheme (I) disagree with published data [14–16] that suggest the unfeasibility of oxidizing the substrate in the absence of oxygen, although they confirm the reaction scheme substantiated in [6, 7, 17].

The effective rate constants found in this way for the oxidation reaction (Table 1) were used to calculate the true rate constants (k_v).

The first rate order with respect to porphyrin and mercaptan in reaction (I) is consistent with published data [6, 18]. The activation energy was calculated by

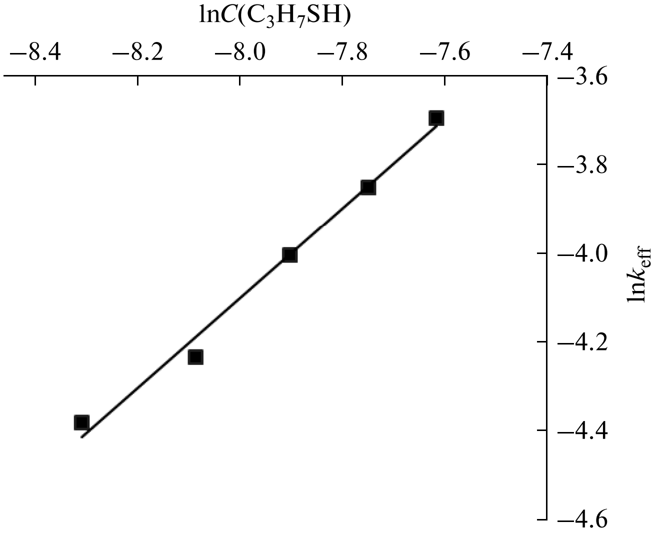


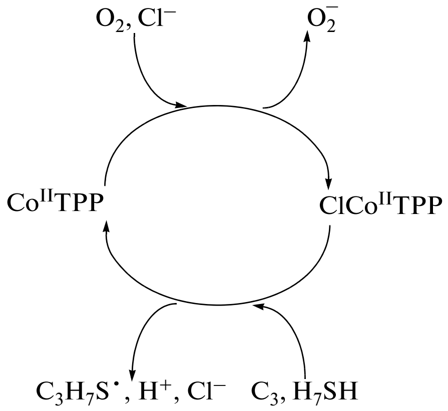
Fig. 3. Dependence of k_{eff} on the n-propyl mercaptan concentration in ethanol. $T = 298.15$ K, and the ClCo$^{\mathrm{II}}$ITPP concentration is 8.11×10^{-6} mol/L.

the least-squares treatment of the linear relationship $\ln k_v = f(1/T)$ (Fig. 4a) using k_v values at several temperatures. The calculated activation parameters are presented in Table 2.

The low value of the activation entropy (−182 J/(mol K)) indicates that the oxidation reaction proceeds through a transition state comprising molecules of the both reactants simultaneously (ClCo$^{\mathrm{III}}$TPP and C_3H_7SH). Apparently, the formation of new bonds and breaking the old bonds of the reactant molecules occurs simultaneously in this transition state. A low activation energy of the process (11.6 kJ/mol) (Table 2) is another point in favor of this assumption. The result of the interaction is the macroheterocycle with reduced cobalt and the radical $C_3H_7S^{\bullet}$, which subsequently combines to give dipropyl disulfide ($C_3H_7SSC_3H_7$).

It was of interest to evaluate the equilibrium constants for the oxidation reaction of n-propyl mercaptan with chloridotetraphenylporphyrinatocobalt(III). Figure 4b shows the temperature dependence of these constants, and Table 2 presents the thermodynamic parameters of the reaction.

The data in Table 2 show that the equilibrium constants of reaction (I) are close to those of the Co$^{\mathrm{II}}$TPP oxidation reaction with molecular oxygen, which means that the both steps are shifted toward the products. In addition, it should be noted that the activation parameters of the oxidation reaction of cobalt(II) tetraphenylporphyrinate with oxygen and reaction (I) are also close (Table 2 and [10]), having a small positive enthalpy (9.7 and 9.2 kJ/mol, respectively) and a high negative entropy (−147 and −182 J/(mol K), respectively). These experimental facts suggest that these reactions can be steps of one redox process, which can be represented by the following scheme:



In the cyclic redox process (Scheme II), the rates of its stages should be equal:

$$-\mathrm{d}[\mathrm{Co^{II}TPP}]/\mathrm{d}\tau = k_{v1}[\mathrm{Co^{II}TPP}][\mathrm{Cl^-}][\mathrm{O_2}], \quad \text{(III)}$$

$$-\mathrm{d}[\mathrm{ClCo^{III}TPP}]/\mathrm{d}\tau = k_{v2}[\mathrm{ClCo^{III}TPP}][\mathrm{RSH}], \quad \text{(IV)}$$

$$k_{v1}[\mathrm{Co^{II}TPP}][\mathrm{Cl^-}][\mathrm{O_2}] = k_{v2}[\mathrm{ClCo^{III}TPP}][\mathrm{RSH}]. \quad \text{(V)}$$

Table 1. Effective and true rate constants and equilibrium constants of oxidation of n-propyl mercaptan with chloridotetraphenylporphyrinatocobalt(III)

C(ClCo$^{\mathrm{III}}$TPP), mol/L	$C(C_3H_7SH)$, mol/L	T, K	k_{eff}, s^{-1}	k_v, L/(mol s)	K_p
$(8.11 \pm 0.39) \times 10^6$	$(3.70 \pm 0.17) \times 10^4$	298.15	$(1.82 \pm 0.05) \times 10^2$	49.2 ± 2.6	$(5.32 \pm 0.45) \times 10^5$
		303.15	$(1.93 \pm 0.05) \times 10^2$	52.2 ± 2.8	$(3.75 \pm 0.33) \times 10^5$
		308.15	$(2.07 \pm 0.06) \times 10^2$	56.0 ± 3.0	$(2.73 \pm 0.25) \times 10^5$
		313.15	$(2.25 \pm 0.05) \times 10^2$	60.8 ± 3.1	$(2.07 \pm 0.19) \times 10^5$
		318.15	$(2.44 \pm 0.06) \times 10^2$	66.0 ± 3.4	$(1.23 \pm 0.11) \times 10^5$

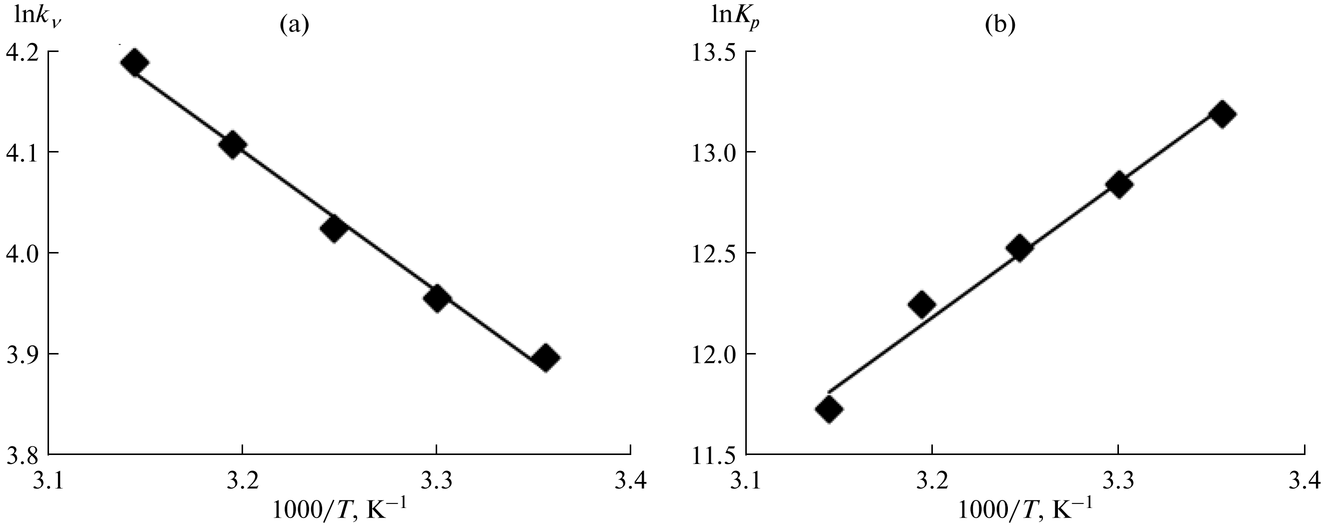


Fig. 4. Plots of the logarithmic (a) rate constant and (b) equilibrium constant versus the inverse temperature in the oxidation of *n*-propyl mercaptan with cobalt(III) tetraphenylporphyrinate.

Table 2. Activation and thermodynamic parameters of the *n*-propyl mercaptan oxidation reaction with chloridotetraphenylporphyrinatocobalt(III) in ethanol at 298.15 K

k_v, L/(mol s)	$\Delta G^\#$, kJ/mol	$\Delta H^\#$, kJ/mol	$\Delta S^\#$, J/(mol K)	E_a, kJ/mol
49.19 ± 2.63	63.3 ± 3.1	9.2 ± 0.7	−182 ± 24	11.6 ± 0.7

K_p	ΔG°, kJ/mol	ΔH°, kJ/mol	ΔS°, J/(mol K)
$(5.32 \pm 0.45) \times 10^5$	−32.7 ± 3.5	−55.5 ± 7.6	−76 ± 11

To calculate the "equilibrium" concentrations [Co^{II}TPP] and [ClCo^{III}TPP], the following input data were selected: $[\mathrm{Co^{II}TPP}] + [\mathrm{ClCo^{III}TPP}] = 1.34 \times 10^5$ mol/L; $[\mathrm{HCl}] = 1.34 \times 10^5$ mol/L; and $[\mathrm{C_3H_7SH}] = 3.70 \times 10^4$ mol/L, as used previously in the experiment. An oxygen concentration of $[\mathrm{O_2}] = 9.80 \times 10^3$ mol/L corresponded to the solubility of oxygen in ethanol under the experimental conditions [19]; $k_{v1} = 2.49 \times 10^3$ L^2/(mol^2 s) [10], $k_{v2} = 49.19$ L/(mol s) (Table 2).

Calculation of the concentrations of the complexes according to Eq. (V) gave the following results:

$$[\mathrm{Co^{II}TPP}]_{\mathrm{equil}} = 1.21 \times 10^{-5} \text{ mol/L};$$

$$[\mathrm{ClCo^{III}TPP}]_{\mathrm{equil}} = 0.13 \times 10^{-5} \text{ mol/L}.$$

This concentration ratio of the Co(II) and Co(III) complexes is due to a higher effective rate constant of step (I), $k_{\mathrm{eff2}} = 1.82 \times 10^{-2}$ s^{-1} at 298.15 K (Table 1), than that of the Co^{II}TPP oxidation step, $k_{\mathrm{eff1}} = 4.47 \times 10^{-6}$ s^{-1} [10]. Nonetheless, the concentrations of Co(II) and Co(III) complexes are comparable, not contradicting the mechanism of the catalytic oxidation of the mercaptan as given by scheme (II).

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