

KINETIC STUDY OF OXYGEN TRANSFER REACTIONS FROM OXO-MONOPEROXO COMPLEXES OF VANADIUM(V) TO THIOLATOCOBALT(III) COMPLEX IN WATER AND CONCENTRATED SOLUTIONS OF ELECTROLYTES

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[Co(en)₂SCH₂CH₂NH₂]²⁺ ion is oxidized to [Co(en)₂SOCH₂CH₂NH₂]²⁺ by the oxo-monoperoxovanadium(V) complexes in aqueous media. These reactions are accompanied by oxygen atom transfer from the peroxo ligand to the coordinated sulfur atom. The relative reactivities for each substrate stand in the order: [VO(O₂)(ada)]⁻ << [VO(O₂)nta]²⁻ ≈ H₂O₂ ≈ [VO(O₂)(H₂O)₄]⁺ < [VO(O₂)(quin)₂]³⁻ << [VO(O₂)(H₂O)₂(pic)], where ada = *N*-(carbamoylmethyl)iminodiacetato(2-), nta = nitrilotriacetato(3-), quin = 2,3-pyridinedicarboxylato(2-) and pic = 2-pyridinecarboxylato(1-) ligands. The effect of pH on the second order rate constant for oxidation by monoperoxo-nta complex is in the pH range 4.8–6.5 consistent with equation $k(298.2\text{ K}) = 0.709 + 1.28 \cdot 10^5 [\text{H}^+]$. Two new oxo-monoperoxo complexes of vanadium(V), NH₄[VO(O₂)(ada)] · H₂O and (NH₄)₃[VO(O₂)(quin)₂] · 3 H₂O, were synthesized and characterized. The salt effects on the thiolatocobalt(III) oxidation by vanadium(V) oxo-monoperoxo complexes as well as by H₂O₂ were studied at 298.2 K in different, up to 5 M solutions of electrolytes. The results can be rationalized in terms of the salt–water interactions.

Key words: Oxo-monoperoxo complexes of vanadium(V); Salt effect; Oxygen transfer reaction.

The study of oxidation of the thiolatocobalt(III) complex by vanadium(V) monoperoxo complexes is a continuation of our previous investigations focused on the medium effect on the oxidation of cobalt(III) complexes with sulfur donor ligands by peroxo compounds^{1,2}. The thiolato complexes are known to react with hydrogen peroxide³ or vanadium(V) peroxo complexes⁴ through a nonradical mechanism. These reactions, often proceeding even at room temperature, obey the S_N2 mechanism involving the oxygen transfer from the peroxo ligand to the nucleophilic sulfur atom coordinated to cobalt(III). The peroxovanadium(V) complexes have been extensively studied from the viewpoint of preparation, crystal structure and as catalysts or stoichiometric oxidants in reactions with organic substrates in organic solvents⁴. Recently, an increased attention is paid to the reactivity of vanadium(V) complexes in aqueous solutions due to the found insulin mimetic effects⁵ and the role of vanadium in the vanadium halogeno-

peroxidases⁶ catalyzing the oxidation of organic substrates in seawater. A better understanding of vanadium chemistry in biological systems requires synthesis of new peroxo complexes of vanadium(V) with N,O donor ligands as models for the study of reactivity. The study of medium effects on kinetics and mechanisms of reactions involving inorganic species frequently include the investigations in binary aqueous–nonaqueous solvents or in aqueous solutions of concentrated electrolytes. As the nonaqueous solvents are not inert to vanadium(V) peroxo complexes⁷, the solvent effects were investigated in aqueous solutions of electrolytes.

In this paper we report the synthesis and characterization of two new vanadium(V) monoperoxo complexes and the kinetics results of the oxygen transfer reactions between monoperoxo-nta, -pic and -quin complexes (nta = nitrilotriacetate, pic = 2-pyridine-carboxylate, quin = 2,3-pyridinedicarboxylate) of vanadium(V) and the thiolato-cobalt(III) complex. In a more limited extent, $[\text{VO}(\text{O}_2)(\text{H}_2\text{O})_4]^+$ and monoperoxo-ada complexes (ada = *N*-(carbamoylmethyl)iminodiacetate) were used as oxidants. The reactivity of the monoperoxo complexes is compared with the corresponding reaction with hydrogen peroxide.

EXPERIMENTAL

Apparatus

The IR spectra in Nujol mulls were registered on a Specord 75 IR spectrometer (Zeiss, Jena). The thermal analysis was performed on a Derivatograph Q 1500 D (MOM, Budapest). ⁵¹V NMR measurements were done on Bruker WP-200 spectrophotometer at 52.64 MHz, chemical shifts are reported with respect to VOCl_3 as external standard. The conductivity was measured by a semiautomatic conductometric bridge of the BM 484 type (Tesla, Brno). The pH was monitored with a Radelkis OP-208 pH-meter fitted with a Radelkis OP-0718 P glass electrode. A Specol 210 spectrometer (Zeiss, Jena) with thermostated (± 0.1 °C) sample compartment was used in kinetic experiments.

Reagents

$(\text{NH}_4)_2[\text{VO}(\text{O}_2)(\text{nta})]$ (ref.⁸), $\text{Ba}[\text{VO}(\text{O}_2)(\text{nta})] \cdot 3 \text{H}_2\text{O}$ (ref.⁹), $[\text{VO}(\text{O}_2)(\text{pic})(\text{H}_2\text{O})_2]$ (ref.¹⁰), $[\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)](\text{ClO}_4)_2$ (ref.¹¹), $[\text{Co}(\text{en})_2(\text{SCH}_2\text{CO}_2)]\text{ClO}_4$ (ref.¹²) were synthesized as described in literature. The synthesis of $\text{NH}_4[\text{VO}(\text{O}_2)(\text{ada})] \cdot \text{H}_2\text{O}$ and $(\text{NH}_4)_3[\text{VO}(\text{O}_2)(\text{quin})_2] \cdot 3 \text{H}_2\text{O}$ is described below. *N*-(Carbamoylmethyl)iminodiacetic acid (H_2ada) from Aldrich, 2,3-pyridinedicarboxylic acid (H_2quin) from Merck and other chemicals from Lachema were of reagent grade. Redistilled, deionized water was used in kinetic measurements.

Preparation of Aqueous Solutions of $\text{H}_2[\text{VO}(\text{O}_2)(\text{nta})]$ and $[\text{VO}(\text{O}_2)(\text{H}_2\text{O})_4]\text{Cl}$

Solution (5 cm³) containing 32.3 mg of $(\text{NH}_4)_2[\text{VO}(\text{O}_2)(\text{nta})]$ was passed through a Dowex X8 ion-exchange resin column (1.5 × 20 cm) (200–400 mesh) in the H⁺ form. The electronic absorption spectrum of $\text{H}_2[\text{VO}(\text{O}_2)(\text{nta})]$ was not changed for about three hours. At the preparation of $\text{H}_2[\text{VO}(\text{O}_2)(\text{nta})]$, $[\text{VO}(\text{O}_2)(\text{H}_2\text{O})_4]^+$ was found as a coproduct (less than 10%). The monoperoxo-aqua complex ($\lambda_{\text{max}} = 455$ nm) was eluted from the column by 1 M HCl.

Synthesis of $(\text{NH}_4)_3[\text{VO}(\text{O}_2)(\text{quin})_2] \cdot 3 \text{H}_2\text{O}$

NH_4VO_3 (0.29 g, 2.5 mmol) was dissolved under cooling in ice bath in a solution of H_2O_2 (3 cm³, 30%) and H_2O (2 cm³). In this solution, solid H_2quin (0.84 g, 5 mmol) was then slowly dissolved. The resulting red solution was filtered and its pH was adjusted to 8.0 with aqueous ammonia (15%) (yellow solution, $\lambda_{\text{max}} = 342 \text{ nm}$). During 10 days, the colour of the solution being kept in refrigerator turned to red. The red monoperoxo-quin complex was isolated on evaporation of the solvent. It was purified by recrystallization from water solution, to which ethanol was added dropwise until a stable turbidity was formed. The product obtained was washed with ethanol and dried at 5 °C in desiccator above silica gel. For $\text{C}_{14}\text{H}_{24}\text{N}_5\text{O}_{14}\text{V}$ (537.2) calculated: 31.27% C, 4.50% H, 13.03% N, 9.48% V; found: 31.10% C, 4.37% H, 13.18% N, 9.44% V. IR spectrum (cm⁻¹): 465 m; 528 m; 552 s, $\nu(\text{V}-\text{O}_{\text{peroxo}})$; 578 m; 610 m; 688 vs; 700 sh; 725 m; 792 m; 815 m; 840 m; 880 m; 925 vs, $\nu(\text{O}-\text{O})$; 948 vs, $\nu(\text{V}=\text{O})$; 1 072 w; 1 114 s; 1 153 m; 1 175 w; 1 237 m; 1 275 vs; 1 395 vs, $\nu_s(\text{COO})$; 1 430 vs, $\delta(\text{NH}_4^+)$; 1 590 vs, 1 615 vs, $\nu_{\text{as}}(\text{COO})$; 1 650 vs, $\delta(\text{H}_2\text{O})$; 1 670 sh. Electronic spectrum of aqueous solution: LMCT ($\text{L} = \text{O}_2^-$) band at 412 nm, $\epsilon = 325 \text{ l mol}^{-1} \text{ cm}^{-1}$. ⁵¹V NMR spectrum of $1 \cdot 10^{-3} \text{ M}$ aqueous solutions at 25 °C: $\delta = -628.93 \text{ ppm}$, band width 284 Hz. Thermal analysis (sample weight 100 mg, the heating rate 2.5 °C min⁻¹): the crystal water is released in an endothermic process in temperature interval 90–150 °C (Δm calculated: 10.1%; found: 11.0%). The active oxygen is released in an exothermic process with maximum at 180 °C.

Synthesis of $\text{NH}_4[\text{VO}(\text{O}_2)(\text{ada})] \cdot \text{H}_2\text{O}$

NH_4VO_3 (0.29 g, 2.5 mmol) was dissolved in cooled solution of H_2O_2 (3 cm³, 30%) and H_2O (30 cm³). In the solution obtained, solid H_2ada (0.47 g, 2.5 mmol) was slowly dissolved under stirring (pH 2). Orange needle shaped crystals of the monoperoxo-ada complex were formed on free crystallization at 5 °C. The product was isolated and dried as for the monoperoxo-quin complex. The pure complex can be prepared within the pH range 2.0–4.5. It is stable for several months when stored in refrigerator. For $\text{C}_6\text{H}_{14}\text{N}_3\text{O}_9\text{V}$ (323.1) calculated: 22.28% C, 4.37% H, 13.00% N, 15.77% V; found: 22.21% C, 4.38% H, 12.98% N, 15.70% V. IR spectrum (cm⁻¹): 425 vw; 495 m; 525 m; 567 s, $\nu(\text{V}-\text{O}_{\text{peroxo}})$; 625 m; 655 m; 685 m; 705 m; 745 s; 810 m; 885 s; 920 vs, $\nu(\text{O}-\text{O})$; 945 vs, $\nu(\text{V}=\text{O})$; 970 m; 1 012 m; 1 105 s, $\nu(\text{C}-\text{N})$; 1 220 m; 1 275 s; 1 315 s; 1 395 vs, $\nu_s(\text{COO})$; 1 420 vs, $\delta(\text{NH}_4^+)$; 1 470 s; 1 610, 1 632 and 1 680 vs, $\nu_{\text{as}}(\text{COO})$, $\nu(\text{CO}-\text{carbamoyl group})$ and $\delta(\text{H}_2\text{O})$. Electronic spectrum of aqueous solution: LMCT ($\text{L} = \text{O}_2^-$) band at 426 nm, $\epsilon = 435 \text{ l mol}^{-1} \text{ cm}^{-1}$. ⁵¹V NMR spectrum of $1 \cdot 10^{-3} \text{ M}$ aqueous solution at 25 °C: $\delta = -547.8 \text{ ppm}$, band width 144 Hz.

Analyses

Contents of C, H and N were determined on a CHN-analyzer (Carlo Erba). Vanadium was estimated gravimetrically as V_2O_5 after heating the sample at 500 °C to constant weight.

Kinetics Studies

The reactions were followed spectrophotometrically at the 370 nm band characteristic of the sulfenato product, $[\text{Co}(\text{en})_2(\text{SOCH}_2\text{CH}_2\text{NH}_2)]^{2+}$. In all kinetic experiments, the monoperoxovanadium(V) complex was used in a 8–10-fold excess over the thiolatocobalt(III) complex. The reactions were initiated by addition of an aliquot of the stock solution of a monoperoxo complex to a thermally equilibrated solution containing other reagents desired. The solution of the monoperoxo-pic complex was used immediately after preparation. Under experimental conditions used, the half-time for oxidation of the thiolatocobalt(III) complex by monoperoxo-pic was 10–23 s. The spectrum of monoperoxo-pic complex was not changed during 5–6 half-times. The rate constants were evaluated by Guggenheim's

method, the values quoted being averages from four different runs. The standard deviations of rate constants, ΔH^\ddagger and of ΔS^\ddagger are given at each value reported. Formate and acetate buffers were used to control pH from 3.0 to 6.5. The spectral studies indicate that complexation of vanadium(V) with components of these buffers is negligible.

Solubilities

The solubilities of $[\text{Co}(\text{en})_2(\text{SCH}_2\text{CO}_2)]\text{ClO}_4$ and $\text{Ba}[\text{VO}(\text{O}_2)(\text{nta})]$. $3 \text{ H}_2\text{O}$ in water and in 4 M solutions of electrolytes were determined by equilibrating an excess of the solid complex with solvent for 5 h at 298.2 K. The concentrations were determined spectrophotometrically at 518 nm ($\epsilon = 152 \text{ l mol}^{-1} \text{ cm}^{-1}$) and 430 nm ($\epsilon = 434 \text{ l mol}^{-1} \text{ cm}^{-1}$), respectively.

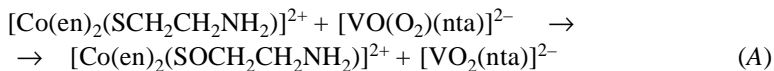
RESULTS

Kinetic Study of Oxidation of $[\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)]^{2+}$ by $[\text{VO}(\text{O}_2)(\text{nta})]^{2-}$

The kinetic data for conversion of the thiolato- to sulfenatocobalt(III) complex by the vanadium(V) monoperoxo oxidant are consistent with the general law given in Eq. (1),

$$-d[[\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)]^{2+}]/dt = k[[\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)]^{2+}][[\text{VO}(\text{O}_2)(\text{nta})]^{2-}] \quad (1)$$

where $[\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)]^{2+}$ and $[\text{VO}(\text{O}_2)(\text{nta})]^{2-}$ are the overall concentrations of complex and oxidant, respectively. The subsequent conversion of the sulfenato to the sulfinato product, $[\text{Co}(\text{en})_2(\text{SO}_2\text{CH}_2\text{CH}_2\text{NH}_2)]^{2+}$, is under our experimental conditions extremely slow. The excess of oxidant leads to the observed first order rate constant, $k_{\text{obs}} = k[\text{VO}(\text{O}_2)(\text{nta})]^{2-}$. In water and in chosen concentrated solutions of electrolytes the k_{obs} is linearly dependent on $[\text{VO}(\text{O}_2)(\text{nta})]^{2-}$ concentration. The control experiments have showed that solutions of monoperoxovanadium(V) complexes under identical experimental conditions but in absence of the substrate are rather stable. The spectral studies demonstrated that in the reaction systems studied, no bond cleavage between vanadium and N,O donor ligand occurred. The stoichiometry of oxidation of the thiolato complex by excess of the vanadium(V) monoperoxo complex (Eq. (A)) is analogous to that of the thiolatocobalt(III)- H_2O_2 reaction¹³.



The effect of $[\text{H}^+]$ on reaction rate was investigated in acetate and formate buffers in the pH range 3.0–6.5 (Table I). The data obtained for the pH range 1.3–2.3 did not follow the first order kinetics. The data found at $\text{pH} \leq 1$ are consistent with first order kinetics, but in this case the oxidant is most probably the $[\text{VO}(\text{O}_2)(\text{H}_2\text{O})_4]^+$ ion,

($k(298.2 \text{ K}) = 1.2 \text{ l mol}^{-1} \text{ s}^{-1}$ in 0.1 M HClO_4). The dependence of rate constants on $[\text{H}^+]$ given in Table I is in accordance with Eq. (2),

$$k = k_1 + k_2[\text{H}^+] \quad (2)$$

which is typical for many oxygen transfer reactions^{13,14}, and where k_1 is the proton independent rate constant and k_2 is the composite rate parameter governing the attack on protonated monoperoxovanadate ion. The efforts to determine the protonation equilibrium constants for $(\text{NH}_4)_2[\text{VO}(\text{O}_2)(\text{nta})]$ and $\text{H}_2[\text{VO}(\text{O}_2)(\text{nta})]$ using potentiometry were unsuccessful owing to the complexities in the chemistry of peroxovanadium(V) species present in acidic solutions. In the potentiometric measurements of the ammonium salt, a similar procedure as in ref.¹⁵ was used. For identification of species in acid medium, ⁵¹V NMR spectra were measured. The spectra exhibit in the pH range 1.8–8.0 only the band of the monoperoxo-nta complex ($\delta = -547.41 \text{ ppm}$). The k is linearly dependent on $[\text{H}^+]$ as in Eq. (2) within a narrow range of $[\text{H}^+]$ (Fig. 1). The extrapolated k_1 values are: $k_1(287.2 \text{ K}) = 0.411 \text{ 0.015}$, $k_1(298.2 \text{ K}) = 0.709 \text{ 0.017}$ and

TABLE I
Kinetic parameters for the oxidation of $[\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)]^{2+}$ by $[\text{VO}(\text{O}_2)(\text{nta})]^{2-}$ in buffered medium^a

pH	$k(287.2 \text{ K})$ $\text{l mol}^{-1} \text{ s}^{-1}$	$k(298.2 \text{ K})$ $\text{l mol}^{-1} \text{ s}^{-1}$	$k(308.7 \text{ K})$ $\text{l mol}^{-1} \text{ s}^{-1}$	ΔH^\ddagger kJ mol^{-1}	ΔS^\ddagger $\text{J K}^{-1} \text{ mol}^{-1}$
3.0 ^b	31.4 ± 1.7	27.9 ± 2.0	21.7 ± 0.3	–	–
3.2 ^b	20.2 ± 0.5	19.1 ± 0.5	20.6 ± 0.3	–	–
3.6 ^{b,c}	6.53 ± 0.20	6.50 ± 0.13	5.76 ± 0.33	–	–
4.0 ^c	3.67 ± 0.06	3.28 ± 0.04	3.43 ± 0.11	–	–
4.4 ^c	1.55 ± 0.02	1.45 ± 0.02	1.87 ± 0.02	–	–
4.6 ^c	0.99 ± 0.03	1.08 ± 0.03	1.42 ± 0.05	–	–
4.8 ^c	0.658 ± 0.020	0.932 ± 0.010	1.31 ± 0.03	21.0 ± 1.2	-175 ± 6
5.0 ^c	0.529 ± 0.017	0.814 ± 0.012	1.18 ± 0.02	25.1 ± 1.2	-163 ± 6
5.2 ^c	0.512 ± 0.010	0.829 ± 0.008	1.18 ± 0.01	27.7 ± 0.9	-154 ± 3
5.8 ^c	0.455 ± 0.020	0.740 ± 0.009	1.13 ± 0.01	30.0 ± 1.6	-147 ± 6
6.5 ^d	0.431 ± 0.004	0.710 ± 0.020	1.09 ± 0.02	27.3 ± 1.5	-156 ± 6

^a Concentrations of $[\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)]^{2+}$ and $[\text{VO}(\text{O}_2)(\text{nta})]^{2-}$: 0.2 and 2.0 mmol l^{-1} , respectively, $I = 0.05 \text{ mol l}^{-1}$; ^b formate buffer; ^c acetate buffer; ^d $[\text{NaClO}_4] = 50 \text{ mmol l}^{-1}$. The rate constants in acetate or formate buffer at pH 3.6 were in range of experimental error identical for all temperatures studied.

$k_1(308.7 \text{ K}) = 1.07 \pm 0.07 \text{ l mol}^{-1} \text{ s}^{-1}$, and the corresponding thermodynamic parameters are: $\Delta H_1^\ddagger = 30.2 \pm 2.5 \text{ kJ mol}^{-1}$ and $\Delta S_1^\ddagger = -147 \pm 8 \text{ J K}^{-1} \text{ mol}^{-1}$. As results from Fig. 1, there is no variation of rate parameters, k_2 , for three temperatures studied. The slopes of plots of k on $[\text{H}^+]$ are: $k_2(287.2 \text{ K}) = (1.43 \pm 0.17) \cdot 10^5$, $k_2(298.2 \text{ K}) = (1.28 \pm 0.12) \cdot 10^5$ and $k_2(308.7 \text{ K}) = (1.43 \pm 0.24) \cdot 10^5 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$. A linear dependence $\ln k = f(1/T)$ was observed only in the pH range 4.8–6.5.

The effect of $[\text{H}^+]$ on oxidation of the thiolato complex by monoperoxo-pic complex was investigated in the pH range 3.0–4.4. The k_{pH} rate constants in acetate buffers at 298.2 K and $I = 0.05 \text{ mol l}^{-1}$ are: $k_{3.0} = 33.2$, $k_{3.6} = 45.0$, $k_{4.0} = 53.1$ and $k_{4.4} = 80.5 \text{ l mol}^{-1} \text{ s}^{-1}$. The approximate value of protonation equilibrium constant for the monoperoxo-pic complex, $K \approx 2 \cdot 10^{-5} \text{ mol l}^{-1}$, was estimated from the pH dependence on concentration of monoperoxo-pic complex at 298.2 K. The extrapolated rate constants, $K_{\text{H}_2\text{O}} \approx 30$ and $k_{\text{OH}^-} \approx 180 \text{ l mol}^{-1} \text{ s}^{-1}$, were estimated by similar procedure as in ref.¹⁶. The $1 \cdot 10^{-2} \text{ M}$ solution of the neutral monoperoxo-pic complex was characterized by conductance $\lambda(298.2 \text{ K}) = 3.1 \text{ S m}^2 \text{ mol}^{-1}$ and pH 3.3.

To compare the oxidizing abilities of the monoperoxo-nta complex with hydrogen peroxide we have reproduced the data published for oxidation of the thiolatocobalt(III) complex by hydrogen peroxide at 298.2 K (ref.¹³). This oxidation was found to be slightly acid dependent, with $k = 1.18 + 1.8 [\text{H}^+]$. The k values obtained from our measurements, $k = (1.08 \pm 0.07) + (1.73 \pm 0.07) [\text{H}^+]$, are in very good agreement with data reported¹³.

Table II shows the values of second order rate constants for the investigated reactions proceeding in water. The neutral monoperoxo-pic complex is roughly 1–3 orders of magnitude more efficient than the anionic vanadium(V) complexes and 50-fold more efficient than hydrogen peroxide. The monoperoxo-ada complex reacts very slowly, the reaction is actually slower than that with hydrogen peroxide.

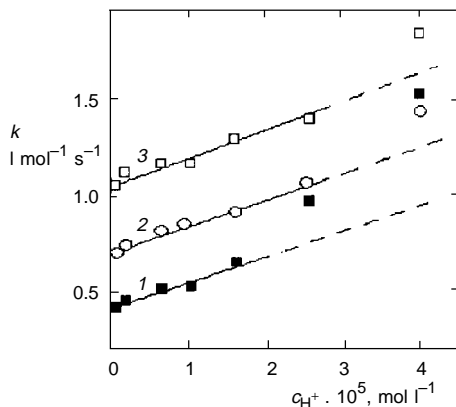


FIG. 1

Plots of k vs $[\text{H}^+]$, for the oxidation of thiolato-cobalt(III) complex by vanadium(V) monoperoxo-nta complex at different temperatures: 1) 287.2 K, 2) 298.2 K; 3) 308.7 K; $c_{\text{thiol}} = 0.2 \text{ mmol l}^{-1}$, $c_{\text{nta}} = 2 \text{ mmol l}^{-1}$, $I = 50 \text{ mmol l}^{-1}$

Effect of Concentrated Solutions of Electrolytes on Rate Constant

The salt effect on oxidation of the thiolatocobalt(III) cation by monoperoxo-nta complex was investigated in aqueous media at pH 6.5, where the rate constant is almost independent on $[H^+]$. In each system, the electrolytes added (LiCl, NaCl, KCl, RbCl, $NaNO_3$ and $NaClO_4$) were found to be inert to the reactants and products. The same conditions were used in oxidations by monoperoxo-pic and -quin complexes as well as by hydrogen peroxide. The experimental results and conditions for four reactions studied in concentrated solutions of electrolytes are summarized in Table III. In 1–4 M concentration range of the salts used as supporting electrolytes, the reaction rates are changed by individual salts in a specific way. The rate constants increase with increasing concentration of electrolytes (positive "salt effect") in oxidation by neutral species, i.e. hydrogen peroxide or monoperoxo-pic complex, though in the latter case there is an exception in the effect of the potassium and rubidium salts. In the oxidation by anionic monoperoxo complexes, quinolinato and nitrilotriacetato, the rate constants decrease with increasing concentration of electrolytes (negative "salt effect") except of LiCl.

Salt Effect on the Solubilities

As results from data in Table IV, the solubility of the monoperoxo-nta complex is higher in concentrated solutions of electrolytes than in water, and unlike the solubility of this complex, the solubility of the mercaptoacetatocobalt(III) complex exhibits only a slight dependence on the nature of electrolyte. As the thiolatocobalt(III) and ammonium salt of monoperoxo-nta complex are very soluble, the less soluble mercaptoacetatocobalt(III) and barium salt of the vanadium(V) monoperoxo-nta complex were used. Based on the similar kinetic behaviour of both cobalt(III) complexes in oxidation by hydrogen peroxide in concentrated solutions of electrolytes (Fig. 2) we assume, that the trend of solubility for both cobalt(III) complexes studied is similar.

TABLE II

Rate constants for the oxidation of $[Co(en)_2(SCH_2CH_2NH_2)]^{2+}$ by different vanadium(V) monoperoxo complexes in water at 298.2 K

Species	$k, 1 \text{ mol}^{-1} \text{ s}^{-1}$	Species	$k, 1 \text{ mol}^{-1} \text{ s}^{-1}$
$[VO(O_2)(H_2O)_2(pic)]$	51.4 ± 1.7	$[VO(O_2)(dipic)(H_2O)]^-$	$(1-3) \cdot 10^{-3,a}$
$[VO(O_2)(ada)]^-$	0.032 ± 0.003	$[VO(O_2)(H_2O)_4]^+$	$\approx 1.4^b$
$[VO(O_2)(nta)]^{2-}$	1.09 ± 0.04	H_2O_2	1.02 ± 0.04
$[VO(O_2)(quin)_2]^{3-}$	5.70 ± 0.03		

^a Taken from the ref.¹³; ^b $[VO(O_2)(H_2O)_4]^+$ was prepared by ion-exchange technique. Reaction followed in 0.1 M HCl.

DISCUSSION

The synthesis of two novel vanadium(V) monoperoxo complexes with N,O donor ligands is reported. The attempts to isolate the monoperoxo-quin complex from acidic solutions containing an excess of H_2O_2 , which are generally used in syntheses of vanadium(V) monoperoxo complexes, failed. The electronic absorption spectrum ($\lambda_{\text{max}} = 342 \text{ nm}$) of

TABLE III

Rate constants for the oxidation of $[\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)]^{2+}$ by H_2O_2 , $[\text{VO}(\text{O}_2)(\text{H}_2\text{O})_2(\text{pic})]$, $[\text{VO}(\text{O}_2)(\text{nta})]^{2-}$ and $[\text{VO}(\text{O}_2)(\text{quin})_2]^{3-}$ at various concentrations of aqueous solutions of electrolytes at 298.2 K

Concentration of electrolyte mol l^{-1}	$k, \text{l mol}^{-1} \text{s}^{-1}$			
	H_2O_2	$[\text{VO}(\text{O}_2)(\text{H}_2\text{O})_2(\text{pic})]$	$[\text{VO}(\text{O}_2)(\text{nta})]^{2-}$	$[\text{VO}(\text{O}_2)(\text{quin})_2]^{3-}$
	LiCl			
0.5	–	27.4 ± 1.0	0.380 ± 0.005	2.63 ± 0.04
1.0	1.53 ± 0.02	24.9 ± 0.9	0.229 ± 0.003	2.30 ± 0.03
2.0	2.14 ± 0.04	31.2 ± 0.6	0.252 ± 0.006	2.54 ± 0.04
3.0	2.77 ± 0.05	35.2 ± 0.9	0.254 ± 0.004	2.87 ± 0.06
4.0	3.72 ± 0.07	49.8 ± 0.8	0.267 ± 0.006	3.45 ± 0.05
5.0	4.85 ± 0.12	–	0.276 ± 0.004	–
	NaCl			
0.5	–	26.1 ± 0.6	0.314 ± 0.005	2.45 ± 0.04
1.0	1.46 ± 0.03	22.9 ± 0.4	0.248 ± 0.003	1.99 ± 0.03
2.0	1.78 ± 0.05	25.6 ± 0.4	0.208 ± 0.004	1.66 ± 0.03
3.0	2.05 ± 0.03	30.4 ± 1.4	0.177 ± 0.003	1.57 ± 0.05
4.0	2.23 ± 0.04	35.4 ± 1.0	0.157 ± 0.004	1.63 ± 0.03
	KCl			
0.5	–	24.5 ± 0.6	0.284 ± 0.003	2.25 ± 0.09
1.0	1.31 ± 0.03	23.4 ± 0.4	0.215 ± 0.005	1.89 ± 0.04
2.0	1.44 ± 0.04	19.9 ± 0.4	0.161 ± 0.003	1.77 ± 0.04
3.0	1.61 ± 0.06	18.9 ± 0.8	0.122 ± 0.003	1.38 ± 0.04
	RbCl			
0.5	–	26.0 ± 0.3	0.225 ± 0.004	1.92 ± 0.05
1.0	1.39 ± 0.03	20.4 ± 0.6	0.188 ± 0.003	1.48 ± 0.04
2.0	1.64 ± 0.03	16.8 ± 0.6	0.133 ± 0.005	1.25 ± 0.06
3.0	1.94 ± 0.04	14.8 ± 0.5	0.105 ± 0.003	1.11 ± 0.03
4.0	2.23 ± 0.07	15.4 ± 0.4	0.085 ± 0.003	0.91 ± 0.03

TABLE III
(Continued)

Concentration of electrolyte mol l ⁻¹	<i>k</i> , l mol ⁻¹ s ⁻¹			
	H ₂ O ₂	[VO(O ₂)(H ₂ O) ₂ (pic)]	[VO(O ₂)(nta)] ²⁻	[VO(O ₂)(quin) ₂] ³⁻
	NaNO ₃			
0.5	–	24.1 ± 0.5	0.330 ± 0.006	2.14 ± 0.09
1.0	1.20 ± 0.04	23.4 ± 0.6	0.264 ± 0.005	1.85 ± 0.08
2.0	1.42 ± 0.03	14.4 ± 0.9	0.201 ± 0.005	1.70 ± 0.08
3.0	1.94 ± 0.02	23.7 ± 0.4	0.165 ± 0.005	1.59 ± 0.02
4.0	2.50 ± 0.03	26.8 ± 1.2	0.128 ± 0.002	1.60 ± 0.06
5.0	3.54 ± 0.10	28.7 ± 1.3	0.108 ± 0.003	1.69 ± 0.03
	NaClO ₄			
0.5	–	24.3 ± 0.5	0.284 ± 0.004	2.30 ± 0.07
1.0	1.02 ± 0.02	23.5 ± 0.5	0.192 ± 0.004	1.86 ± 0.03
2.0	0.99 ± 0.02	26.6 ± 1.2	0.143 ± 0.003	1.68 ± 0.05
3.0	1.11 ± 0.03	31.7 ± 0.6	0.087 ± 0.004	1.76 ± 0.04
4.0	1.20 ± 0.03	42.2 ± 1.9	0.053 ± 0.003	1.67 ± 0.03

Concentrations of [Co(en)₂(SCH₂CH₂NH₂)]²⁺, [VO(O₂)(nta)]²⁻, [VO(O₂)(quin)₂]³⁻, [VO(O₂)(H₂O)₂(pic)] and H₂O₂: 0.2, 2.0, 2.0, 1.6 and 28.1 mmol l⁻¹, respectively.

TABLE IV
Solubilities of Ba[VO(O₂)(nta)] · 3 H₂O and [Co(en)₂(SCH₂COO)]ClO₄ in water and in concentrated solutions of electrolytes at 298.2 K

Electrolyte ^a	Solubility, mmol l ⁻¹	
	Ba[VO(O ₂)(nta)] · 3 H ₂ O	[Co(en) ₂ (SCH ₂ COO)]ClO ₄
H ₂ O	2.72	34.0
LiCl	8.81	71.0
NaCl	16.5	62.6
RbCl	45.8	63.6
NaNO ₃	72.5	74.6
NaClO ₄	17.0	–

^a *c* = 4 mol l⁻¹.

the reaction solution indicates a presence of a diperoxo-quin complex of vanadium(V) (ref.¹⁷). The red monoperoxo-quin complex is formed in solution by slow decomposition of the yellow diperoxo species.

The optimum pH of reaction solution for preparation of $(\text{NH}_4)[\text{VO}(\text{O}_2)(\text{ada})] \cdot \text{H}_2\text{O}$ was found to be 2.0–4.5, although “in situ” the monoperoxo-ada complex is formed in the wide pH range 1.1–8.6 (ref.¹⁸).

Based on comparison of the IR spectrum of $(\text{NH}_4)_3[\text{VO}(\text{O}_2)(\text{quin})_2] \cdot 3 \text{H}_2\text{O}$ with spectrum of dipotassium 2,3-pyridinedicarboxylate, the bands at 522 and 925 cm^{-1} could be unambiguously assigned to $\nu(\text{V}-\text{O}_{\text{peroxo}})$ and $\nu(\text{O}-\text{O})$ stretchings, respectively. The comparison of IR spectrum of $(\text{NH}_4)[\text{VO}(\text{O}_2)(\text{ada})] \cdot \text{H}_2\text{O}$ with IR data for $\text{K}_2\text{ada} \cdot \text{H}_2\text{O}$ allowed to assign the same stretchings in the monoperoxo-ada complex at 567 and 920 cm^{-1} , respectively. The $\nu(\text{V}-\text{O}_{\text{peroxo}})$ and $\nu(\text{O}-\text{O})$ bands in both complexes are at wavelengths characteristic for vanadium(V) monoperoxo complexes, which all were found by X-ray analysis to have a pentagonal bipyramidal arrangement around vanadium atom. The $\nu_{\text{s+as}}(\text{COO})$ band positions and missing of $\nu(\text{COOH})$ band in IR spectrum of $(\text{NH}_4)[\text{VO}(\text{O}_2)(\text{ada})] \cdot \text{H}_2\text{O}$ indicate a coordination of the ada ligand via two deprotonated carboxylate groups and imino nitrogen atom, the latter by shift of the (C–N) band position to lower wavenumbers¹⁹ (1 105 cm^{-1} in complex compared with 1 142 cm^{-1} in $\text{K}_2\text{ada} \cdot \text{H}_2\text{O}$).

Oxidation of Thiolatocobalt(III) by Vanadium(V) Monoperoxo Complexes

The second order kinetics and large negative ΔS^\ddagger value (Table I) substantiate the conclusion that the investigated reactions proceed via an $\text{S}_{\text{N}}2$ path as do the redox reactions of nucleophiles with peroxides^{3,20}. The negative value of ΔS^\ddagger is ascribed to a highly oriented transition state and provide a strong evidence for an associative mechanism for the peroxovanadium(V)–thiolatocobalt(III) reaction. The nucleophilic substitution is connected with transfer of oxygen to the sulfur atom of the thiolato ligand. In these

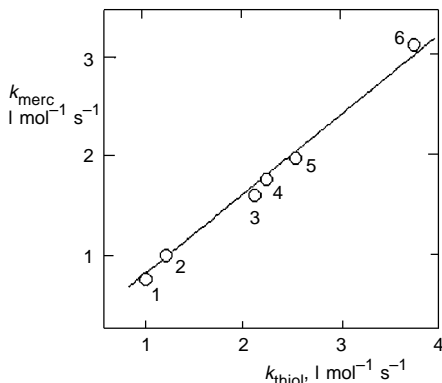


FIG. 2

Relationship between k_{merc} for the mercaptoacetato-cobalt(III) complex and k_{thiol} for thiolatocobalt(III) complex oxidation by hydrogen peroxide in electrolyte solutions: 1 H_2O , 2 NaClO_4 , 3 LiClO_4 , 4 NaNO_3 , 5 NaCl , 6 LiCl ; $c_{\text{merc}} = c_{\text{thiol}} = 0.2 \text{ mmol l}^{-1}$, $c_{\text{H}_2\text{O}_2} = 28.1 \text{ mmol l}^{-1}$, $c_{\text{electrolyte}} = 4 \text{ mol l}^{-1}$, $c_{\text{HClO}_4} = 1 \text{ mmol l}^{-1}$, $T = 298.2 \text{ K}$

oxidations, the transferred oxygen atom originates from the peroxy ligand, since the reduced dioxovanadium(V) species is inactive¹⁰. The source of oxygen in the sulfenato cobalt product, $[\text{Co}(\text{en})_2\text{SOCH}_2\text{CH}_2\text{NH}_2]^{2+}$, was examined by means of ^{18}O tracer experiments and the oxygen atom transferred was found to originate from the peroxy ligand²¹. The following structure of the transition state can thus be proposed:

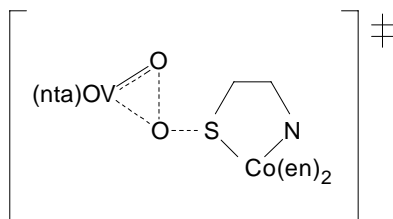


Table II shows that the rate constant is markedly dependent on the nature of the N,O donor ligand. A further effect, which may influence the reaction rate, is a possible different stabilisation of the transition state through hydrogen bond between oxygen atom of the oxo or carboxylato ligands of the monoperoxo complex and the $-\text{NH}_2$ group of the thiolato complex under favourable steric conditions.

It was previously shown that the oxidation of thiolatocobalt(III) by vanadium(V) monoperoxo complex is slower than by a vanadium(V) diperoxo species¹⁵. According to data given in Table II, the reactivity of monoperoxo-pic complex is higher than that of the diperoxo analogue¹⁵, ($k_{[\text{VO}(\text{O})_2\text{pic}]^{2-}} = 13 \text{ l mol}^{-1}\text{s}^{-1}$ at 298.2 K and pH 6.1).

Effect of pH on Oxidation of Thiolatocobalt(III) by Vanadium(V) Monoperoxo Complexes

The effect of pH on the second order rate constant can be reasonably attributed to chemistry involving the monoperoxo complex, because the thiolato cobalt(III) complex does not participate in an acid-base equilibrium. The rate increase with pH decreasing from 6.5 to 4.8 is attributable to acid catalyzed path involving the protonated and deprotonated forms of the monoperoxo-nta complex. The protonation of this complex has been observed by indirect but rather convicting kinetic evidence (Fig. 1). The k_2 is a composite rate parameter which includes the protonation equilibrium constant of the monoperoxo-nta complex, an information on this constant is, however, not available. According to data in refs^{15,22}, the acid catalysis in oxidation of vanadium(V) monoperoxo complexes arises from reactive species presumably protonated at the peroxy group. The greater rate constant for the protonated form is consistent with this proposal.

The activation enthalpy and entropy decrease with decreasing pH (Table I). This effect can be regarded as a result of change of the acid-base equilibrium constant of the oxidant with temperature. From the decrease of ΔH^\ddagger we deduce that the enthalpy of this

acid-base equilibrium is negative, and is included in the activation enthalpy. The extrapolated value, ΔH_1^\ddagger , for the deprotonated form of oxidant is nearly the same as for oxidation by hydrogen peroxide¹³. At $\text{pH} < 4.8$ the experimental values of rate constants (Table I) are not consistent with Eq. (2) for all temperatures studied and the dependence $\log k = f(1/T)$ is not consistent with Arrhenius equation.

The rate of thiolatocobalt(III) oxidation by vanadium(V) monoperoxo-pic complex is pH dependent. In spite of the narrow pH interval the changes of rate constants with pH were significant. One of the tentative hypotheses is that there is an equilibrium between neutral aqua- and anionic hydroxo-pic complex of vanadium(V) in water. The study of the most reactive monoperoxo-pic complex showed that its acid-base behaviour, in water characterized by a conductance Λ and pH, is similar to a weak acid like the acetic acid. In the monoperoxo-pic complex, a pentagonal bipyramidal environment around vanadium with significant hydrogen bonding between the peroxo moiety and the equatorial water molecule was found¹⁰. Therefore, a dissociation of hydrogen atom from water in equatorial position is probable.

Effect of Concentrated Solutions of Electrolytes on Rate Constants

According to the Brønsted–Bjerrum theory, the primary salt effect derived from coulombic interactions manifests itself in diluted electrolytes. Besides this effect, another “salt effect” occurs in concentrated electrolytes ($c > 1 \text{ mol l}^{-1}$), due to the decrease of effective water concentration resulting from ion–solvent molecule interactions. This “salt effect” can be more important than the primary salt effect if concentrated electrolytes are used^{23,24}. The results given in Table III for four different redox reactions with common substrate confirm the existence of a specific “salt effect” with magnitude depending upon the nature of a salt. The dependence of $\ln k$ on electrolyte concentration c can be written in the form of Eq. (3)

$$\ln k = \ln k_0 + Sc, \quad (3)$$

where Sc is accounting for the ion–solvent interactions and k_0 is an empirical parameter. For all electrolytes studied, $\ln k$ varies linearly with salt concentrations $c > 1 \text{ mol l}^{-1}$ as shown in Fig. 3. Such linear correlations were found for all reactions studied except of the oxidation by monoperoxo-quin in NaNO_3 solution. As can be seen from Table III, a positive “salt effect” was found in LiCl both in neutral molecule–cation and anion–cation reactions. For the chlorides, the sequence of rate constants is: $k(\text{Li}^+) > k(\text{Na}^+) > k(\text{K}^+) \geq k(\text{Rb}^+)$. The correlation based on the linear relationship of Gibbs’ energies (Figs 4 and 5) shows that the same effects are operating in different reactions, independently on the charge of reactants and that an explanation based only on a participation of associated forms

of the reactants with ions of supporting electrolytes would not be satisfactory. Our observations are in agreement with expected decrease of association between oppositely charged ions with increasing ionic strength in concentrated electrolytes²⁵. The main cause of kinetic salt effects observed in concentrated solutions of electrolytes is the interaction between supporting electrolyte and solvent. The hydration of electrolytes introduced into the system causes a decrease of water activity and consequently could lead to change in solvation of the initial and transition states. The extent of the electrolyte hydration depends on the charge to size ratio. An additional information on solute-water interaction is given by the change of reactant solubilities on going from water to concentrated electrolytes (Table IV). The nitrilotriacetato complex solubility shows a "salting in" effect. The solubility values, s , increase in the order: $s(\text{LiCl}) < s(\text{NaCl}) < s(\text{RbCl})$, while the rate constants are in an inverse order (Table III). The

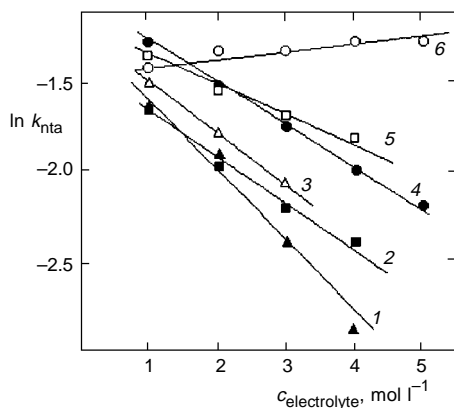


FIG. 3
Plots of $\ln k_{\text{nta}}$ vs $c_{\text{electrolyte}}$ for the oxidation of thiolatocobalt(III) complex by vanadium(V) monoperoxo-nta complex: 1 NaClO_4 , 2 RbCl , 3 KCl , 4 NaNO_3 , 5 NaCl , 6 LiCl ; $c_{\text{thiol}} = 0.2 \text{ mmol l}^{-1}$, $c_{\text{nta}} = 2 \text{ mmol l}^{-1}$, $T = 298.2 \text{ K}$

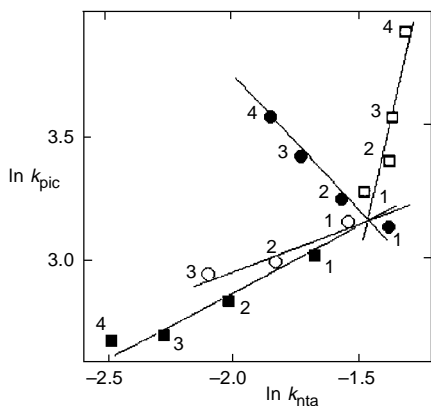


FIG. 4
Plots of $\ln k_{\text{pic}}$ vs $\ln k_{\text{nta}}$ at 298.2 K. The individual points correspond to following electrolyte concentrations (mol l^{-1}): 1 1, 2 2, 3 3, 4 4; \blacksquare RbCl , \circ KCl , \bullet NaCl , \square LiCl . The values of rate constants are taken from Table III

solubility of mercaptoacetato cobalt(III) complex, which was used as a model compound, is almost independent on the nature of supporting electrolyte. As follows from these facts, the changes of solvation of the initial state as well as of the reaction rates in concentrated electrolytes are mainly connected with the monoperoxo-nta complex.

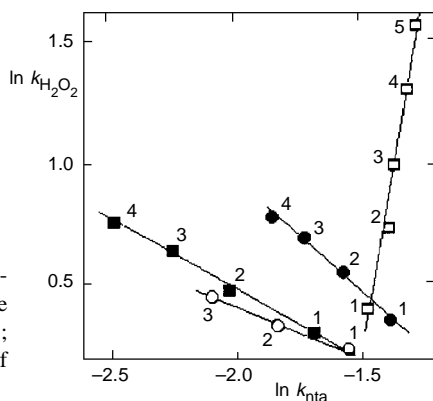


FIG. 5

Plots of $\ln k_{\text{H}_2\text{O}_2}$ vs $\ln k_{\text{nta}}$ at 298.2 K. The individual points correspond to following electrolyte concentrations (mol l^{-1}): 1 1, 2 2, 3 3, 4 4, 5 5; ■ RbCl, ○ KCl, ● NaCl, □ LiCl. The values of rate constants are taken from Table III

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