

Possibilities of using some correlation relations based on linear relationship of the Gibbs energies for studying the oxidation of ligands of some cobalt(III) complexes

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Dedicated to Professor E. Treindl, DrSc., in honour of his 60th birthday

In order to appreciate the reaction mechanism in a series of oxidations of the ligands bonded in Co(III) complexes by different oxidizing agents such as IO_4^- , $\text{S}_2\text{O}_8^{2-}$, and H_2O_2 , the correlations based on the principle of linear relationship of the Gibbs energies were used. The results obtained for oxidation of the ions $[\text{CoCyS}(\text{en})_2]^+$, $[\text{CoCySO}(\text{en})_2]^+$, $[\text{Co}(\text{en})_2\text{SCH}_2\text{COO}]^+$, $[\text{Co}(\text{NH}_3)_5\text{NCS}]^{2+}$, and $[\text{Co}(\text{dmgH})_2(\text{NCS})_2]^-$ were completed by the results concerning the oxidation of the $[\text{Co}(\text{en})_2\text{SOCH}_2\text{COO}]^+$ ion by periodate.

При изучении механизма реакций окисления ряда лигандов в комплексах трехвалентного кобальта различными окислительными агентами, как IO_4^- , $\text{S}_2\text{O}_8^{2-}$ и H_2O_2 были использованы корреляции, основанные на принципе линейного соотношения между свободными энергиями. Результаты, полученные при изучении окисления комплексных ионов $[\text{CoCyS}(\text{en})_2]^+$, $[\text{CoCySO}(\text{en})_2]^+$, $[\text{Co}(\text{en})_2\text{SCH}_2\text{COO}]^+$, $[\text{Co}(\text{NH}_3)_5\text{NCS}]^{2+}$ и $[\text{Co}(\text{dmgH})_2(\text{NCS})_2]^-$, были дополнены данными о кинетике окисления иона $[\text{Co}(\text{en})_2\text{SOCH}_2\text{COO}]^+$ периодатом.

The investigation of oxidation kinetics of the Co(III) complex ions, *i.e.* $[\text{CoCyS}(\text{en})_2]^+$, $[\text{CoCySO}(\text{en})_2]^+$, $[\text{Co}(\text{en})_2\text{SCH}_2\text{COO}]^+$, $[\text{Co}(\text{dmgH})_2(\text{NCS})_2]^-$, and $[\text{Co}(\text{NH}_3)_5\text{NCS}]^{2+}$ by the use of different oxidizing agents such as IO_4^- , H_2O_2 , and $\text{S}_2\text{O}_8^{2-}$ has shown that the reaction rate and the thermodynamic activation parameters change in dependence on pH of medium [1–10]. The greatest changes in these reaction parameters were observed for the oxidation by periodate [4–6, 10]. A similar effect manifests itself in the oxidation of other substrates by periodate as well [11, 12]. Periodate in solution is subjected to rather complicated acid–base and hydration equilibria [13, 14] owing to which it may occur in different forms, especially as IO_4^- , H_4IO_6^- , H_5IO_6 , and $\text{H}_3\text{IO}_6^{2-}$, while the predominating form of periodate is dependent on pH of medium. It has been found that the IO_4^- ion is the most reactive form. As far as the oxidation by hydrogen peroxide is concerned [1, 8], more significant change in reaction rate was observed only for the medium of $\text{pH} < 1$. On the other hand, the smallest change in reaction rate with pH was observed for the oxidation by peroxodisulfate [3, 7].

These reactions obey the S_N2 mechanism which involves a transfer of oxygen atom of the oxidizing agent to the nucleophilic sulfur of ligand in the Co(III) complex. The acid—base equilibria of reactants and especially of the oxidizing agent affect the reaction rate and the mechanism of reaction, which can show itself in the correlation relations, based on linear relationship of the Gibbs energies [15—17].

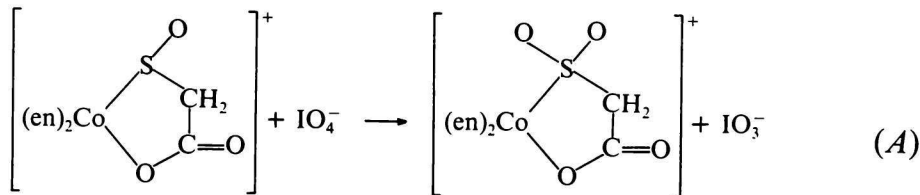
The aim of this study has been to appreciate the possibility of using the correlation relations for investigating the influence of acid—base equilibria on reaction mechanism of the mentioned oxidations.

Experimental

As for the kinetic measurements, we started from bis(ethylenediamine)mercaptoacetato-cobalt(III) perchlorate which was prepared in an analogous way as cysteinatobis(ethylenediamine)cobalt(III) perchlorate [18]. A sufficient excess of the oxidizing agent, *i.e.* NaIO_4 was used in order that the first reaction stage might proceed very rapidly and the reaction rate of the second stage, *i.e.* the oxidation of the bis(ethylenediamine)mercaptosulfenatocobalt(III) ion by periodate could be investigated. The working procedure was like described in paper [5] for the oxidation of the cysteinatobis(ethylenediamine)cobalt(III) ion by periodate to the second stage.

Results and discussion

The oxidation of $[\text{Co}(\text{en})_2\text{SOCH}_2\text{COO}]^+$ by periodate obeys the following scheme



This reaction is governed by the next rate equation similarly as the oxidation of $[\text{Co}(\text{en})_2\text{SCH}_2\text{COO}]^+$

$$\frac{-d[[\text{Co}(\text{en})_2\text{SOCH}_2\text{COO}]^+]}{dt} = k_{\text{obs}}[\text{IO}_4^-][[\text{Co}(\text{en})_2\text{SOCH}_2\text{COO}]^+] \quad (I)$$

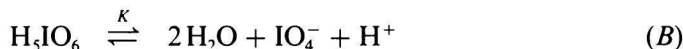
where $[[\text{Co}(\text{en})_2\text{SOCH}_2\text{COO}]^+]$ and $[\text{IO}_4^-]$ are analytical concentrations of reactants. The dependence of rate constant and activation parameters ΔH^\ddagger and ΔS^\ddagger on HClO_4 concentration is given in Table 1.

Table 1

Dependence of the rate constant, ΔH^\ddagger , and ΔS^\ddagger on HClO_4 concentration for the oxidation of $[\text{Co}(\text{en})_2\text{SOCH}_2\text{COO}]^+$ by periodate
 $c([\text{Co}(\text{en})_2\text{SOCH}_2\text{COO}]^+) = 2 \times 10^{-4} \text{ mol dm}^{-3}$, $c(\text{IO}_4^-) = 1.2 \times 10^{-2} \text{ mol dm}^{-3}$,
 $I = 0.112 \text{ mol dm}^{-3}$, $T = 298.2 \text{ K}$

$c(\text{HClO}_4)$ mol dm^{-3}	$k \cdot 10$ $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	ΔH^\ddagger kJ mol^{-1}	ΔS^\ddagger $\text{J mol}^{-1} \text{ K}^{-1}$
0.100	0.95 ± 0.012	85.5 ± 2.1	26 ± 6
0.050	1.38 ± 0.03	79.0 ± 1.5	4 ± 4
0.030	1.81 ± 0.03	71.1 ± 1.2	-21 ± 4
0.010	2.54 ± 0.05	60.7 ± 1.4	-55 ± 4
0.005	2.85 ± 0.04	58.4 ± 1.9	-59 ± 4
0.003	3.04 ± 0.04	58.0 ± 1.8	-60 ± 6
0.001	3.12 ± 0.04	58.0 ± 1.9	-60 ± 6

The changes in rate constant and activation parameters ΔH^\ddagger and ΔS^\ddagger are especially related with acid—base equilibrium of the oxidizing agent, *i.e.* periodate which follows the following equation



From the value of dissociation constant K [13] the values of equilibrium concentration of IO_4^- and H_5IO_6 were calculated for different concentrations of perchloric acid. The dependence of k_{obs} on equilibrium concentration of IO_4^- was linear and its extrapolation to the zero concentration of IO_4^- enabled us to determine the rate constant $k_{\text{H}_5\text{IO}_6} = (3.84 \pm 0.25) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298.2 K. The rate constant $k_{\text{IO}_4^-} = (0.322 \pm 0.016) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298.2 K was determined from the relationship $k_{\text{obs}} = f([\text{IO}_4^-]_{\text{eq}})$ by using the extrapolation to analytical concentration of the oxidizing agent. A similar method was described in the paper [5]. The temperature dependence of the extrapolated rate constants was used for determining the activation parameters $\Delta H_{\text{IO}_4^-}^\ddagger = (56.4 \pm 1.9) \text{ kJ mol}^{-1}$, $\Delta S_{\text{IO}_4^-}^\ddagger = (-65 \pm 4) \text{ J mol}^{-1} \text{ K}^{-1}$, $\Delta H_{\text{H}_5\text{IO}_6}^\ddagger = (99.8 \pm 6.6) \text{ kJ mol}^{-1}$, and $\Delta S_{\text{H}_5\text{IO}_6}^\ddagger = (63 \pm 18) \text{ J mol}^{-1} \text{ K}^{-1}$. The change in activation enthalpy $\Delta\Delta H^\ddagger = (\Delta H_{\text{H}_5\text{IO}_6}^\ddagger - \Delta H_{\text{IO}_4^-}^\ddagger)$ was equal to 43 kJ mol^{-1} . Equal change $\Delta\Delta H^\ddagger$ was also observed in the case of oxidation of $[\text{CoCyS}(\text{en})_2]^+$ [4], $[\text{CoCySO}(\text{en})_2]^+$ [5], $[\text{Co}(\text{en})_2\text{SCH}_2\text{COO}]^+$ [6], and $[\text{Co}(\text{NH}_3)_5\text{NCS}]^{2+}$ [10] by

periodate. The value $\Delta\Delta H^\ddagger$ is comparable with ΔH_{dis} [13] for the equilibrium according to scheme (B). On the basis of this fact we may assume that the activation enthalpy ΔH^\ddagger includes ΔH_{dis} for H_5IO_6 .

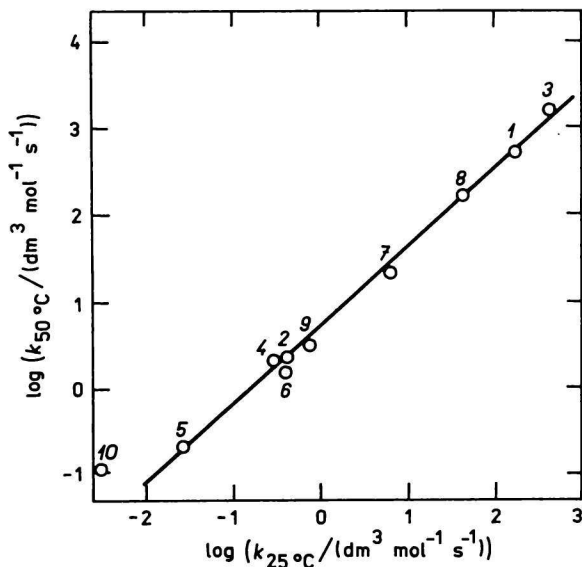


Fig. 1. Relationship $\log k_{50^\circ\text{C}} = f(\log k_{25^\circ\text{C}})$ for a series of oxidations of ligands bonded in the Co(III) complexes in the medium of 10^{-3} M-HClO₄. Individual points correspond to the

- | | | |
|--|----------------------|---|
| 1. $[\text{CoCyS}(\text{en})_2]^+ + \text{IO}_4^-$; | following reactions: | 6. $[\text{CoCyS}(\text{en})_2]^+ + \text{H}_2\text{O}_2$; |
| 2. $[\text{CoCySO}(\text{en})_2]^+ + \text{IO}_4^-$; | | 7. $[\text{CoCyS}(\text{en})_2]^+ + \text{S}_2\text{O}_8^{2-}$; |
| 3. $[\text{Co}(\text{en})_2\text{SCH}_2\text{COO}]^+ + \text{IO}_4^-$; | | 8. $[\text{Co}(\text{en})_2\text{SCH}_2\text{COO}]^+ + \text{S}_2\text{O}_8^{2-}$; |
| 4. $[\text{Co}(\text{en})_2\text{SOCH}_2\text{COO}]^+ + \text{IO}_4^-$; | | 9. $[\text{Co}(\text{en})_2\text{SCH}_2\text{COO}]^+ + \text{H}_2\text{O}_2$; |
| 5. $[\text{Co}(\text{NH}_3)_5\text{NCS}]^{2+} + \text{IO}_4^-$; | | 10. $[\text{Co}(\text{dmgH})_2(\text{NCS})_2]^- + \text{S}_2\text{O}_8^{2-}$. |

For appreciating the influence of acid—base equilibria on oxidation of the Co(III) complexes we used the correlation relations based on the principle of linear relationships of the Gibbs energies [14—17]. Figs. 1 and 2 represent the correlation $\log k_{T_1} = f(\log k_{T_2})$ for a series of oxidations of ligands bonded in the Co(III) complexes at 10^{-3} M-HClO₄ (Fig. 1) and 10^{-1} M-HClO₄ (Fig. 2). In the medium of 10^{-3} M-HClO₄ the experimental points satisfy a correlation, the correlation coefficient being $r = 0.998$. Point 10 which corresponds to the oxidation of $[\text{Co}(\text{dmgH})_2(\text{NCS})_2]^-$ by peroxodisulfate is out of the correlation straight line. In this oxidation the mechanism is more complicated [9], it is not only a simple transfer of oxygen atom without cleavage of the central ion—ligand bond because the high value $\Delta H^\ddagger = 113 \text{ kJ mol}^{-1}$ indicates that the central ion—ligand bond is simultaneously split. At this concentration of HClO₄ all used oxidizing agents as well as complexes are in the deprotonated state.

In the medium of 10^{-1} M-HClO₄ (Fig. 2) points 1—6 (for the most part corresponding to the oxidation by periodate) are in good correlation, $r = 0.997$, while other three points are out of this straight line. Points 7—9 correspond to those reactions in which the rate constant varied within the range of experimental error in the above-mentioned interval of HClO₄ concentrations. This fact gives evidence that the difference between reactivities of the protonated and deprotonated form of reactant is small.

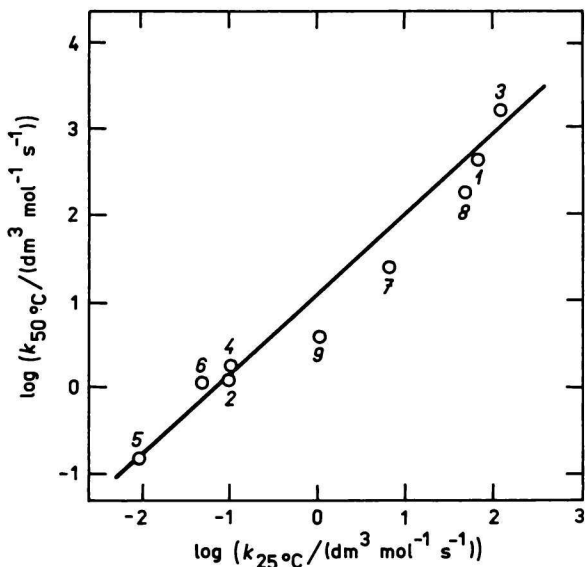


Fig. 2. Relationship $\log k_{50^\circ\text{C}} = f(\log k_{25^\circ\text{C}})$ ($r = 0.997$) for the series of reactions given in Fig. 1 in the medium of 10^{-1} M-HClO₄. Denotation of points like in Fig. 1.

Figs. 3 and 4 represent the correlation relations of the oxidation of $[\text{Co}(\text{en})_2\text{SCH}_2\text{COO}]^+$ and $[\text{CoCyS}(\text{en})_2]^+$ by periodate in which the points on the plots $\log k_{T_1} = f(\log k_{T_2})$ correspond to different concentrations of perchloric acid taking part in the mentioned reactions. In this case, the correlation relations result from acid—base equilibrium of periodate the protonated and deprotonated forms of which significantly differ from each other in their reactivity. Straight line *a* corresponds to the interval of HClO₄ concentrations in which the oxidizing agent occurs predominantly in the form of H₅IO₆, while straight line *b* corresponds to the HClO₄ concentrations in which the oxidizing agent is present predominantly in the form of IO₄⁻. At a lower acid concentration it is the IO₄⁻ ion that attacks the substrate while at a higher acid concentration the attack of the IO₄⁻ ion takes place only after dehydration and deprotonation of H₅IO₆. In this case the acid—base equilibrium of $[\text{CoCyS}(\text{en})_2]^+$

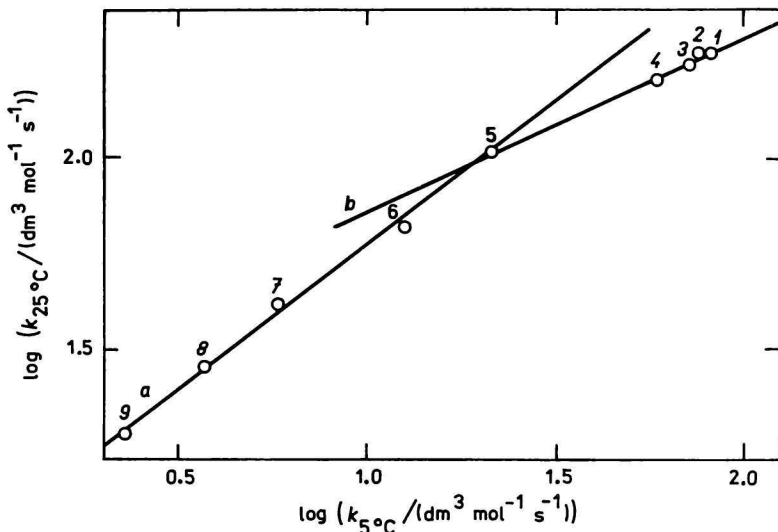


Fig. 3. Relationship $\log k_{25^\circ\text{C}} = f(\log k_{5^\circ\text{C}})$ ($r_a = 0.998$, $r_b = 0.997$) for the oxidation of $[\text{CoCyS}(\text{en})_2]^+$ by periodate. Individual points correspond to the following concentrations of perchloric acid: 1. 10^{-3} ; 2. 3×10^{-3} ; 3. 5×10^{-3} ; 4. 10^{-2} ; 5. 5×10^{-2} ; 6. 10^{-1} ; 7. 2×10^{-1} ; 8. 3×10^{-1} ; 9. $5 \times 10^{-1} \text{ mol dm}^{-3}$. $I = 0.501 \text{ mol dm}^{-3}$.

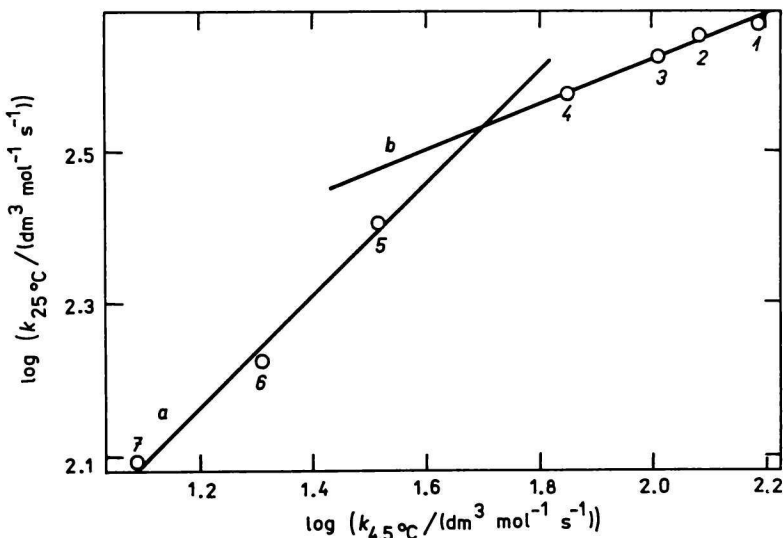


Fig. 4. Relationship $\log k_{25^\circ\text{C}} = f(\log k_{4.5^\circ\text{C}})$ ($r_a = 0.998$, $r_b = 0.996$) for the oxidation of $[\text{Ce}(\text{en})_2\text{SCH}_2\text{COO}]^+$ by periodate. Individual points correspond to the following concentrations of perchloric acid: 1. 10^{-3} ; 2. 3×10^{-3} ; 3. 5×10^{-3} ; 4. 10^{-2} ; 5. 3×10^{-2} ; 6. 5×10^{-2} ; 7. $10^{-1} \text{ mol dm}^{-3}$. $I = 0.101 \text{ mol dm}^{-3}$.

does not manifest itself in the correlation relation (Fig. 3) because the difference between reactivities of the protonated and nonprotonated form of the complex ion is negligible when compared with the change in reactivity of the oxidizing agent [4]. Such linear correlations as in Figs. 3 and 4 were not more observed for the oxidations of $[\text{CoCySO}(\text{en})_2]^+$ and $[\text{Co}(\text{en})_2\text{SOCH}_2\text{COO}]^+$ by periodate because an opening of the chelate ring of ligand may also take place in the course of oxidation to the second stage, in particular at higher HClO_4 concentration [19]. No linear correlation was found for the oxidation of $[\text{CoCyS}(\text{en})_2]^+$ by peroxodisulfate and hydrogen peroxide. In this case the reaction rate is approximately to an equal extent affected by the acid—base equilibria of both reactants. The least change in reaction rate produced by varying pH of medium was observed for the oxidation by peroxodisulfate. It resulted from the fact that the protonation did not take place on the peroxidic oxygen which immediately attacked the nucleophilic sulfur of ligand in the Co(III) complex.

In conclusion we may state that the correlation $\log k_{T_1} = f(\log k_{T_2})$ is valid for the series of oxidations of the Co(III) complexes which follow equal mechanism in a medium where both reactants are present in the deprotonated form. Similar correlations have also been observed for other types of reactions which obey common mechanism, e.g. aquation of chelate ligands of the Co(III) complexes [20] and substitution reactions of the pentacyanoiron(II) complexes [21]. If the reaction rate is significantly influenced by the acid—base equilibrium of single reactant, two pH intervals can be found for a given reaction where the correlation is linear. If more influences are effective for a given reaction and none of them is dominant, the relation $\log k_{T_1} = f(\log k_{T_2})$ cannot be correlated with the change of pH.

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