Solvent Effect on the Kinetics of Oxidation of [Co(en)$_2$SCH$_2$COO]$^+$ by Periodate in Water—Methanol and Water—*tert*-Butanol Mixture

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Solvent effect on the oxidation of [Co(en)$_2$SCH$_2$COO]$^+$ by IO$_4^-$ in aqueous mixtures of methanol and *tert*-butanol was studied. The transfer Gibbs energy of activation $\Delta G_t^\neq$ increased monotonously with increasing cosolvent content, however the changes of $\Delta H_t^\neq$ and $T\Delta S_t^\neq$ showed almost the mirror course. The changes in solvation on going from initial to the transition state were discussed on the basis of the transfer functions of ΔG_t°, ΔH_t°, and $T\Delta S_t^\circ$. The transfer enthalpies of reactants were evaluated from calorimetric measurements. The values of ΔH_t° and $T\Delta S_t^\circ$ corresponding to the initial and transition states exhibited an extreme at $x_2 \approx x_2^\neq$ cosolvent mole fraction.

The reaction of [Co(en)$_2$SCH$_2$COO]$^+$ with IO$_4^-$ in aqueous solutions belongs to a relatively small group of the reactions of the complex ions, in which the nucleophilic substitution with transfer of oxygen from the oxidant to sulfur is connected with the formation of S—O bond without the interruption of Co—ligand bond [1—4]. The decrease of the rate constant with increasing medium acidity for the investigated reaction was due to the formation of less reactive form of the oxidant H$_5$IO$_6$. The effect of cosolvent was discussed using the Wells's assumption [4], which is based on the Born's electrostatic model of solvation, $\Delta G_t^\circ(H^+)$ and the extrathermodynamic assumption [3], which is based on the equality of contributions of the transfer function from the large unipositive and uninegative ions, usually tetraphenylarsonium Ph$_4$As$^+$ or tetraphenylphosphonium Ph$_4$P$^+$ and tetraphenylborate Ph$_4$B$^-$, $\Delta G_t^\circ(\text{Ph}_4\text{As}^+) = \Delta G_t^\circ(\text{Ph}_4\text{P}^+) = \Delta G_t^\circ(\text{Ph}_4\text{B}^-)$, to the transfer function of salt.

In the present paper, we dissected the transfer Gibbs energies of initial and transition states on the enthalpic and entropic contributions in order to obtain the more detailed analysis of solvent effect on the kinetics of the reaction under investigation.

EXPERIMENTAL

All chemicals used were of anal. grade: NaIO$_4$, *tert*-butanol (Reanal, Budapest), and methanol (Lachema, Brno); [Co(en)$_2$SCH$_2$COO]ClO$_4$ was prepared according to [1] (elemental analysis corresponded to the calculated values). Methanol and *tert*-butanol were redistilled before use. The enthalpies of solution ΔH_s° of NaIO$_4$ were measured in the con-

centration range 1×10^{-3}—5×10^{-3} mol dm^{-3} using an isoperibolic calorimeter (constructed in Technical University, Brno) as described earlier [5]. The values ΔH_s° were found to be independent of salt concentration within the experimental scatter, so they were taken as the standard values. The experimental data are averages of five to six independent measurements. The standard deviations of the measured ΔH_s° are given at each reported value (Table 1).

Table 1. Enthalpies of Solution ΔH_s° of NaIO$_4$ in the H$_2$O—MeOH and H$_2$O—*t*-BuOH Mixtures at 298.2 K

x_2(MeOH)	ΔH_s°(NaIO$_4$) kJ mol^{-1}	x_2(*t*-BuOH)	ΔH_s°(NaIO$_4$) kJ mol^{-1}
0	32.9 ± 0.2	0	32.9 ± 0.2
0.047	36.5 ± 0.2	0.021	42.8 ± 0.7
0.100	40.7 ± 0.4	0.046	50.2 ± 0.2
0.160	41.9 ± 0.7	0.076	47.2 ± 0.2
0.228	40.4 ± 0.3	0.113	42.6 ± 0.5

RESULTS AND DISCUSSION

The oxidation of [Co(en)$_2$SCH$_2$COO]$^+$ by IO$_4^-$ proceeds *via* S$_N$2 mechanism with transfer of oxygen from the oxidant to the nucleophilic sulfur of the mercaptoacetate ligand [4]. The kinetics of this oxidation were studied in detail in aqueous mixtures with MeOH and *t*-BuOH [4]. In 1×10^{-3} mol dm^{-3} HClO$_4$, IO$_4^-$ form prevails and the decrease of reaction rate with increasing cosolvent content reflects especially the change of interaction between solvent molecules in both mixtures under investigation.

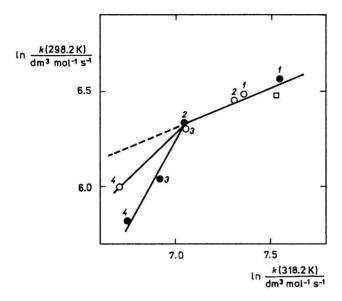The correlation dependence ln k(298 K) = f(ln k(318 K)) (Fig. 1) based on the linear relationship

Fig. 1. Dependence ln k(298 K) = f(ln k(318 K)) for oxidation of $[Co(en)_2SCH_2COO]^+$ by IO_4^-. Individual points correspond to the following mole fractions of cosolvent x_2. □ Water, ● water—t-BuOH: *1*. 0.021, *2*. 0.046, *3*. 0.076, *4*. 0.113. ○ Water—MeOH: *1*. 0.047, *2*. 0.100, *3*. 0.160, *4*. 0.228. The values of the rate constants are taken from Ref. [4].

of free energies [6], in which the experimental points correspond to the different cosolvent mole fraction x_2, shows the discontinuity at x_2^* where the cosolvent influence on the enhancement of the three-dimensional water structure occurs. At $x_2 > x_2^*$ the equilibrium composition between the free solvent molecules and the solvent molecules bonded in the clathrates changes gradually towards the former ones. Fig. 1 shows the different behaviour of methanol and *tert*-butanol. Although both the solvents belong to typically aqueous ($G^E > 0$, $|H^E| < |TS^E|$) [7], the specific water—cosolvent interactions affect the reactivity of reactants through different change of their solvation.

Some information about the solute—solvent interaction provide the values of the enthalpy of solution ΔH_s° (Table 1). The values of ΔH_s° include the crystal lattice energy of the solute, the energy necessary for formation of the cavity in the solvent to accomodate the solute and enthalpy associated with resolvation. The transfer enthalpy ΔH_t°(salt) = ΔH_s°(salt)$_{x_2}$ − ΔH_s°(salt)$_{H_2O}$ includes only two last contributions: the endothermic cavity term and the exothermic term associated with the solute resolvation. The sign of ΔH_t° estimates which term is dominant.

The transfer enthalpies of reactants were calculated using the data for $\Delta H_t^\circ(Na^+)$ and $\Delta H_t^\circ(ClO_4^-)$ for mixtures water with MeOH [8] and t-BuOH [9, 10]. The values of $\Delta H_t^\circ([Co(en)_2SCH_2COO]^+)$ and

Table 2. Transfer Functions ΔH_t° and TAS_t° for IO_4^- (*a*) and $[Co(en)_2SCH_2COO]^+$ (*b*) in the Water—MeOH and Water—t-BuOH Mixtures at 298.2 K

Solvent	x_2	ΔH_t°/(kJ mol^{-1})		TAS_t°/(kJ mol^{-1})	
		a	b*	a	b*
MeOH	0.047	4.4	− 5.4	4.6	− 6.1
	0.100	6.7	1.6	7.5	0.2
	0.160	5.2	8.0	5.7	5.5
	0.228	2.2	5.3	1.8	1.9
t-BuOH	0.021	7.7	5.1	7.8	3.8
	0.046	2.8	18.4	2.7	17.0
	0.076	1.7	15.1	0.8	14.7
	0.113	3.9	5.4	2.1	4.9

*Values from Ref. [11].

$\Delta H_t^\circ(IO_4^-)$ (Table 2) were calculated as difference between transfer functions of ΔH_t°(salt) and $\Delta H_t^\circ(ClO_4^-)$ or $\Delta H_t^\circ(Na^+)$. In water—MeOH the positive values of $\Delta H_t^\circ(IO_4^-)$ corresponding to the cavity formation were observed, $\Delta H_t^\circ(IO_4^-)$ being maximal at $x_2^* \approx 0.15$ where the maximum structural arrangement of solvent occurs. The similar trend, which reflects mainly solvent—solvent interactions was observed also for the complex ion in both investigated mixtures (Table 2). The dependence $\Delta H_t^\circ(IO_4^-)$ = f($x_2(t$-BuOH)) indicates that in this case the ion—solvent interaction takes place in a great extent and this exothermic effect causes the decrease of $\Delta H_t^\circ(IO_4^-)$ values at $x_2^*(t$-BuOH) ≈ 0.05. From comparison of ΔH_t°(anion) for IO_4^- and for the other oxidant $S_2O_8^{2-}$ it is evident that the cavity term is dominant for the former ion, but for the $S_2O_8^{2-}$ the resolvation term is dominant ($\Delta H_t^\circ(S_2O_8^{2-}) < 0$) [11]. These effects are connected probably with the different charge of anion.

The TAS_t° values (Table 2) were calculated from transfer Gibbs energies ΔG_t° and ΔH_t° for corresponding ions. The values of ΔG_t° were determined from the solubilities of salts under standard conditions [3]. The low values of ΔG_t° for both ions in the H_2O—t-BuOH mixture and for IO_4^- in H_2O—MeOH result from the compensation of large changes of enthalpic and entropic terms (Table 2). The change of $\Delta G_t^\circ([Co(en)_2SCH_2COO]^+)$ is governed by the enthalpic term at higher cosolvent content.

The activation parameters of oxidation of $[Co(en)_2SCH_2COO]^+$ by IO_4^- are significantly influenced by the addition of cosolvent [4]. The change of activation enthalpy is due to the solvation change of initial (is) and transition (ts) states according to the equation

$$\Delta H_t^{\ddagger} = \Delta H^{\ddagger}(x_2) - \Delta H^{\ddagger}(H_2O) =$$
$$= \Delta H_t^\circ(ts) - \Delta H_t^\circ(is) \quad (1)$$

ΔH_t°(is) is expressed by the following equation

$$\Delta H_t^\circ(is) = \Delta H_t^\circ([Co(en)_2SCH_2COO]^+) +$$
$$+ \Delta H_t^\circ(IO_4^-) \quad (2)$$

The same relations apply for $T\Delta S_t^{\ddagger}$. In both investigated mixtures, with the exception of $x_2 = 0.047$ for H_2O—MeOH, the $\Delta H_t^{\circ}(is)$ decrease (Table 3) is due to more significant destabilization of the initial

Table 3. Activation Transfer Functions $\Delta H_t^{\ddagger}$ and $T\Delta S_t^{\ddagger}$ and Transfer Functions of the Initial State $\Delta H_t^{\circ}(is)$, $T\Delta S_t^{\circ}(is)$ for Oxidation of [Co(en)₂SCH₂COO]⁺ by IO_4^- in the H_2O—MeOH and H_2O—t-BuOH Mixtures at 298.2 K

Solvent	x_2	$\Delta H_t^{\ddagger a}$	$\Delta H_t^{\circ}(is)$	$T\Delta S_t^{\ddagger}$	$T\Delta S_t^{\circ}(is)$
		kJ mol⁻¹	kJ mol⁻¹	kJ mol⁻¹	kJ mol⁻¹
MeOH	0.047	− 7.0	− 1.0	− 6.9	− 1.5
	0.100	− 7.5	8.3	− 7.5	7.7
	0.160	− 12.0	13.2	− 12.5	11.2
	0.228	− 12.9	7.5	− 14.3	3.7
t-BuOH	0.021	− 2.5	12.8	− 2.1	11.6
	0.046	− 13.3	21.2	− 13.7	19.7
	0.076	− 6.6	16.8	− 7.7	15.5
	0.113	− 4.5	9.3	− 6.0	7.0

a) The values of $\Delta H_t^{\ddagger}$ are evaluated from activation enthalpies published in Ref. [4].

state in comparison to the transition one. At $x_2(\text{MeOH}) = 0.047$ both initial and transition states are stabilized. The stabilization of initial state is determined mainly by MeOH—[Co(en)₂SCH₂COO]⁺ interaction, $\Delta H_t^{\circ}([\text{Co(en)}_2\text{SCH}_2\text{COO}]^+) < 0$ (Table 2). In spite of this favourable change of $\Delta H_t^{\ddagger}$, the overcompensating contribution from $T\Delta S_t^{\ddagger}$ leads to

$\Delta G_t^{\ddagger} > 0$ and the reaction rate decreases with the increasing content of nonaqueous solvent. The importance of ion—solvent interaction in the kinetics of the reaction studied can be seen from comparison of [Co(en)₂SCH₂COO]⁺ oxidation by IO_4^- and $S_2O_8^{2-}$ [11] in the H_2O—t-BuOH mixture. In this mixture the different behaviour of oxidant leads to an opposite effect of cosolvent on the rate constant. The comparison of dependences $\Delta H_t^{\circ}(ts) = f(\varphi_2)$ (Fig. 2) for both the reactions mentioned at $\varphi_2(t\text{-BuOH}) \approx 20$ vol. % $\approx x_2^{\ast}$ shows that for oxidation by IO_4^- the uncharged activated complex (Formula 1) is more destabilized than the negative one for the oxidation by $S_2O_8^{2-}$.

Formula 1

The different trend of $\Delta H_t^{\circ}(ts)$ dependences (Fig. 2) in H_2O—MeOH is connected with different behaviour of both cosolvents. According to [12, 13], methanol in contrast to t-BuOH can participate in water structure and produce the binary clusters in which MeOH acts as proton acceptor, whereas the water molecules act as the proton donor.

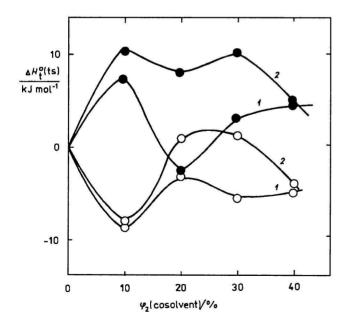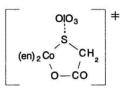**Fig. 2.** Dependence of the transfer enthalpy of the transition state $\Delta H_t^{\circ}(ts)$ for oxidations of [Co(en)₂SCH₂COO]⁺ by $S_2O_8^{2-}$ (*1*) and by IO_4^- (*2*) on the cosolvent volume fraction; ○ H_2O—MeOH, ● H_2O—t-BuOH.

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