THERMODYNAMIC AND KINETIC INVESTIGATION OF THE SOLVENT EFFECT ON THE OXIDATION OF $[Co(en)_2SCH_2COO]^+$ WITH $S_2O_8^{2-}$ IN WATER–METHANOL AND WATER–TERT-BUTYL ALCOHOL MIXTURES

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Received April 23, 1992
Accepted October 29, 1992

Dedicated to Professor Vladislav Holba in honour of his 60th birthday.

The kinetics of oxidation of $[Co(en)_2SCH_2COO]^+$ with $S_2O_8^{2-}$ was studied in water–methanol and water–tert-butyl alcohol mixtures. Changes in the reaction activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ with varying concentration of the co-solvent depend on the kind of the latter, which points to a significant role of solvation effects. The solvation effect on the reaction is discussed based on a comparison of the transfer functions ΔH_t^0, ΔS_t^0 and ΔG_t^0 for the initial and transition states with the changes in the activation parameters accompanying changes in the co-solvent concentration. The transfer enthalpies of the reactants were obtained from calorimetric measurements.

When investigating reaction kinetics in aqueous–nonaqueous mixtures, the changes in the kinetic parameters occurring on varying the concentration of the nonaqueous solvent are usually discussed in terms of the transfer functions of the reactants and of the activated complex[1]. The solvation effects have mostly been only examined based on changes in the Gibbs transfer functions[2 – 4]. Oxidation of $[Co(en)_2SCH_2COO]^+$ with $S_2O_8^{2-}$ in a mixed system of water with tert-butyl alcohol (t-BuOH) has been studied in ref.[5], where the difference between the Gibbs transfer functions of the initial and transition states was found to change only slightly with the co-solvent concentration. A more detailed analysis of the solvation effects can be made by comparing the transfer enthalpies and entropies of the initial and transition states. This approach has so far been applied to a limited extent, e.g. in refs[6 – 9].

In the present work we obtained additional kinetic data in the water–methanol (MeOH) mixed medium, the heats of solution of the reactants were measured in the two mixed media, and the effect of the nonaqueous component of the solvent on the reaction was analyzed based on the transfer functions ΔH_t^0, ΔS_t^0 and ΔG_t^0.

EXPERIMENTAL

All the chemicals were of reagent grade purity. The $[Co(en)_2SCH_2COO]ClO_4$ complex was prepared as described in the literature[10]. Methanol and tert-butyl alcohol were redistilled prior to use. The kinetic measurement procedure has been reported[5]. The heats of solution were measured on an isoperibolic calorimeter (Technical University, Brno); its calibration and the heat measurement have been given in ref.[11]. The concentration region for the measurements of the heats of solution was 2 to 20 mmol dm^{-3}. Across this region, the experimental heats of solution were constant to within the precision of determination of the ΔH_s^0 value. For this reason, the data measured were regarded as the standard enthalpies of solution. The ΔH_s^0 values are averages of 5 to 6 independent measurements; their errors are given in Table I.

RESULTS AND DISCUSSION

Oxidation of $[Co(en)_2SCH_2COO]^+$ with $S_2O_8^{2-}$ proceeds through the S_N2 mechanism, which is associated with oxygen transfer from the oxidant to the nucleophilic sulfur of the mercapto acetate ligand[5]. The reaction rate in the H_2O–t-BuOH system increases with increasing concentration of co-solvent, whereas the reverse is true in the H_2O–MeOH system (Table II). The activation parameters are affected appreciably by the addition of the co-solvent, particularly in the H_2O–MeOH system. The activation enthalpy adopts its minimum value at the co-solvent mole fraction $x_2 = x_2^*$, at which the structure of water is arranged to the highest degree due to the co-solvent present[12,13]. The change in the activation enthalpy is related to the change in the solvation of the initial state (is) and of the transition state (ts) according to Eq. (*1*).

TABLE I
Enthalpies of solution, ΔH_s^0 of $K_2S_2O_8$ and $[Co(en)_2SCH_2COO]ClO_4$ in H_2O–MeOH and H_2O–t-BuOH mixtures at 298.2 K

x_2	ΔH_s^0, kJ mol^{-1}	
	$K_2S_2O_8$	$[Co(en)_2SCH_2COO]ClO_4$
	MeOH	
0	63.1 ± 0.8	32.8 ± 0.1
0.047	67.3 ± 0.6	31.3 ± 0.2
0.100	70.7 ± 0.3	38.4 ± 0.1
0.160	70.4 ± 0.3	43.7 ±0.1
0.228	64.4 ± 0.5	39.9 ± 0.1
	t-BuOH	
0.021	72.2 ± 0.5	41.3 ± 0.1
0.046	75.7 ± 0.4	48.6 ± 0.3
0.076	72.2 ± 0.6	45.2 ± 0.2
0.113	67.7 ± 0.5	38.0 ± 0.3

$$\Delta H_t^{\neq} = \Delta H^{\neq}(x_2) - \Delta H^{\neq}(H_2O) = \Delta H_t^0(ts) - \Delta H_t^0(is) \qquad (1)$$

$$\Delta H_t^0(is) = \Delta H_t^0([Co(en)_2SCH_2COO]^+) + \Delta H_t^0(S_2O_8^{2-}) \qquad (2)$$

The transfer enthalpies of the reactants in Eq. (*2*) were obtained from the heats of solution of the salts (Table I). The transfer function of the salts was calculated from Eq. (*3*).

$$\Delta H_t^0(\text{salt}) = \Delta H_S^0(\text{salt}, x_2) - \Delta H_S^0(\text{salt}, H_2O) \qquad (3)$$

The ion transfer enthalpies $\Delta H_t^0([Co(en)_2SCH_2COO]^+)$ and $\Delta H_t^0(S_2O_8^{2-})$ were obtained by subtracting $\Delta H_t^0(K^+)$ and $\Delta H_t^0(ClO_4^-)$, respectively, from the transfer function of the respective salt. The values of the transfer functions $\Delta H_t^0(K^+)$ and $\Delta H_t^0(ClO_4^-)$, which were determined based on the TPTB assumption (TPTB is tetraphenylphosphonium tetraphenylborate; $\Delta H_t^0(Ph_4P^+) = \Delta H_t^0(Ph_4B^-)$) were taken from ref.[14] for the H_2O–MeOH system and from refs[15,16] for the H_2O–t-BuOH system, for which the TATB assumption was used (TATB = tetraphenylarsonium tetraphenylborate; $\Delta H_t^0(Ph_4As^+) = \Delta H_t^0(Ph_4B^-)$). The transfer enthalpies of the ions examined, along with the $T\Delta S_t^0$ values,

TABLE II

Rate constants and thermodynamic activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ of the oxidation of $[Co(en)_2SCH_2COO]^+$ with $S_2O_8^{2-}$ in dependence on the mole fraction (x_2) of MeOH and t-BuOH in mixtures with water at 298.2 K. Concentrations of $HClO_4$, $[Co(en)_2SCH_2COO]^+$ and $Na_2S_2O_8$: 1.0, 0.0585 and 0.768 mmol dm^{-3}, respectively

x_2	k, $dm^3\ mol^{-1}\ s^{-1}$	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta S^{\neq}$, J $mol^{-1}\ K^{-1}$
		MeOH	
0	106 ± 3	40.2 ± 1.3	-71 ± 6
0.047	105 ± 2	31.6 ± 1.5	-100 ± 5
0.100	93 ± 2	27.6 ± 1.0	-105 ± 4
0.160	82 ± 1	24.4 ± 1.0	-116 ± 4
0.228	74 ± 1	26.4 ± 1.1	-109 ± 4
		t-BuOH	
0.021	105 ± 2	37.2 ± 1.5	-81 ± 6[a]
0.046	105 ± 3	37.0 ± 1.4	-82 ± 6[a]
0.076	121 ± 2	39.9 ± 1.0	-71 ± 4[a]
0.113	143 ± 2	42.2 ± 1.3	-62 ± 6[a]

[a] Data from ref.[5]

are given in Table III. The ΔS_t^0 values were calculated from the Gibbs transfer functions ΔG_t^0 of the ions[17]. While the ΔG_t^0 values vary monotonically with the concentration of co-solvent and the positive values indicate their destabilization due to the presence of the latter, the dependences of the ΔH_t^0 and $T\Delta S_t^0$ values exhibit extremes whose positions primarily mirror the effect of interactions between the solvent molecules. The transfer enthalpy ΔH_t^0 involves the exothermic effect associated with the resolvation of the ion, and the endothermic effect associated with the formation of a cavity in the three-dimensional structure of the solvent. The ΔH_t^0 values in Table III indicate that at the co-solvent mole fraction $x_2 \approx x_2^*$ the exothermic effect only predominates for the $S_2O_8^{2-}$ anion in the H_2O–t-BuOH system. A similar effect has been observed in this system for other anions as well[18]. The ΔH_t^0(ion) values were used to calculate the transfer functions of the initial state ΔH_t^0(is) by Eq. (*2*) (Table IV). It can be inferred from a comparison of the ΔH_t^* values with the ΔH_t^0(is) and ΔH_t^0(ts) values (Fig. 1) that the decrease in the activation enthalpy in the H_2O–t-BuOH system is related to the higher destabilization of the initial state as compared to the transition state. The change in the ΔH_t^* value is considerably higher in the H_2O–MeOH system than in the H_2O–t-BuOH system. In this case the decrease in ΔH_t^* is related not only to the destabilization of the initial state but also to the stabilization of the activated complex (Fig. 1). In spite of this favourable change in ΔH_t^*, the reaction rate in the H_2O–MeOH system

TABLE III

Transfer functions ΔH_t^0 and $T\Delta S_t^0$ from water to H_2O–MeOH and H_2O–t-BuOH mixtures for $S_2O_8^{2-}$ (a) and $[Co(en)2SCH2COO]_4^+$ (b) at 298.2 K in dependence on the mole fraction (x_2) of MeOH and t-BuOH in aqueous solutions

x_2	ΔH_t^0, kJ mol^{-1}		$T\Delta S_t^0$, kJ mol^{-1}	
	a	b	a	b
		MeOH		
0.047	6.6	-5.4	6.4	-6.1
0.100	7.0	1.6	6.1	0.2
0.160	1.1	8.0	0.0	5.5
0.228	-9.5	5.3	-12.4	1.9
		t-BuOH		
0.021	5.2	5.1	4.2	3.8
0.046	-17.7	18.4	-19.8	17.0
0.076	-11.8	15.1	-18.5	14.7
0.113	-3.1	5.4	-13.4	4.9

TABLE IV

Transfer activation parameters $\Delta H_t^{\neq}$ and $T\Delta S_t^{\neq}$ and transfer functions of the initial state ΔH_t^0(is) and $T\Delta S_t^0$(is) (all in kJ mol^{-1}) for the oxidation of $[Co(en)_2SCH_2COO]^+$ with $S_2O_8^{2-}$ in H_2O–MeOH and H_2O–t-BuOH mixtures at 298.2 K

$S_2O_8^{2-}$ + $[Co(en)_2SCH_2COO]^+$				
x	$\Delta H_t^{\neq}$	ΔH_t^0(is)	$T\Delta S_t^{\neq}$	$T\Delta S_t^0$(is)
		MeOH		
0.047	-8.6	1.2	-8.6	0.3
0.100	-12.6	8.6	-13.1	6.3
0.160	-15.8	9.1	-16.4	5.5
0.228	-13.8	-4.2	-14.3	-10.5
		t-BuOH		
0.021	-3.0	10.3	-3.0	8.0
0.046	-3.2	0.7	-3.3	-2.8
0.076	-0.3	3.3	0.0	-3.8
0.113	2.0	2.3	2.7	-8.5

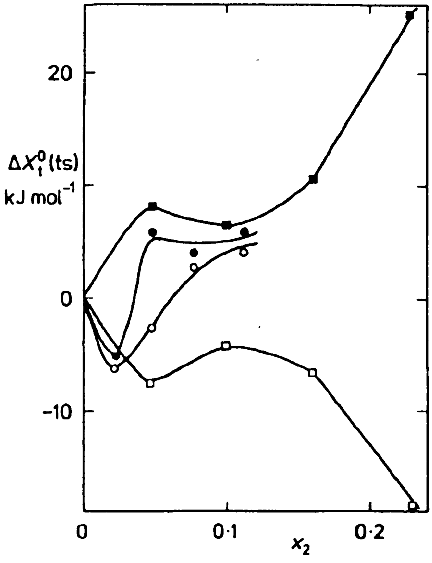

FIG. 1

Thermodynamic transfer functions of the transition state, ΔH_t^0(ts) (○, □) and $T\Delta S_t^0$(ts) (●, ■) for the oxidation of $[Co(en)_2SCH_2COO]^+$ with $S_2O_8^{2-}$, in H_2O–MeOH (□, ■) and H_2O–t-BuOH (○, ●) mixtures, in dependence on the mole fraction of the non-aqueous co-solvent at 298.2 K decreases, which is due to the prevailing effect of the entropy term, so that the total change in the two activation parameters, $\Delta H_t^{\neq}$ and $T\Delta S_t^{\neq}$, leads to an increase in the Gibbs transfer activation energy with increasing concentration of co-solvent. In the H_2O–t-BuOH system the changes in the $\Delta H_t^{\neq}$ and $T\Delta S_t^{\neq}$ values lead to a change in $\Delta G_t^{\neq}$ with increasing concentration of co-solvent, owing to which the reaction rate increases. The experimental results indicate that the different effect of co-solvent on the reaction rate primarily mirrors the different behaviour of the oxidant in the H_2O–MeOH and H_2O–t-BuOH mixtures.

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Translated by P. Adámek.