

Investigation of the effect of organic solvents on kinetic parameters in metal catalyzed reactions

LJILJANA TRIFKOVIĆ and GORDANA A. MILOVANOVIĆ*

Faculty of Chemistry, University of Belgrade, P. O. Box 158, YU-11001 Belgrade, Yugoslavia

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The effects of acetone and acetonitrile on the kinetic parameters of azorubin S oxidation by hydrogen peroxide catalyzed by manganese(II), pyrocatechol violet oxidation by hydrogen peroxide catalyzed by copper(II), and carminic acid oxidation by hydrogen peroxide catalyzed by copper(II) and activated by bifenox, were examined. It was established that the examined solvents exhibit various effects on the kinetic parameters of the above said reactions. In all instances a change in the solvent concentration affects both the enthalpy and the entropy contributions to the free activation energy during the transition of the system into the active state, as well as the constant of the active complex formed at this point.

Keywords: kinetics, metal catalyzed reactions, acetone, acetonitrile, azorubin S, pyrocatechol violet, carminic acid, hydrogen peroxide.

INTRODUCTION

In a previous papers¹ it was reported that in the presence of acetone (4.1 mol dm⁻³) the sensitivity of the oxidation of azorubin S by hydrogen peroxide, catalyzed by manganese(II), was increased, and that in the presence of acetonitrile (5.7 mol dm⁻³) both the sensitivity and the selectivity of the oxidation of pyrocatechol violet by hydrogen peroxide, catalyzed by copper(II), were also increased. In addition, it was established that the activating effect of the herbicide bifenox on copper(II) was more pronounced in aqueous solution of acetone (0.14 mol dm⁻³).² The kinetics of these reactions were studied.

In this paper the effects of acetone and acetonitrile on kinetic parameters of the reactions mentioned above were investigated.

Recently, the effect of acetone-dimethylformamide mixtures on the kinetic parameters of the copper(II) catalyzed oxidation of carminic acid activated by endosulfan were examined.³

EXPERIMENTAL

Apparatus

The reaction rate was followed with a Specol 20MA-9508 spectrophotometer (Iskra). The temperature was kept constant with an ultrathermostat type NBE (VEB Prüferate-Werk, Medingen). The pH-measurements were performed by means of a Radiometer 4C pH-meter.

* Serbian Chemical Society active member.

Reagents

Analytical grade reagents and redistilled water were used. The stock solutions were of the following concentrations (mol dm^{-3}): azorubin S (Merck), 1.0×10^{-5} ; pyrocatechol violet (Merck), 1.0×10^{-3} ; carminic acid (BDH), 6.1×10^{-5} ; hydrogen peroxide (Merck), 9.8; sodium hydrogen carbonate (Merck), 0.2; potassium carbonate and potassium hydrogen carbonate (Merck), 1.0; manganese (II) sulphate (Merck), copper(II) sulphate (Merck) and bifenox (Rhône-Pulenc), 1.0×10^{-2} ; acetone (Merck), acetonitrile (Merck). The borate buffer (pH 8.65 0.1 mol dm^{-3}) was prepared by mixing $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{ H}_2\text{O}$ (Reanal) and NaOH (Merck).

Procedure

Solutions of azorubin S, pyrocatechol violet or carminic acid and buffer were measured into one compartment, hydrogen peroxide into the second and manganese(II), copper(II) or bifenox, acetone or acetonitrile and water up to a total volume of 25 cm^3 into the third compartment of a special reaction vessel,⁴ and brought to a definite temperature (288.15 K, 293.15 K, 298.15 K and 303.15 K). The reaction was then started by mixing the solutions.

The initial reagents concentrations were (mol dm^{-3}): azorubin S, 4.0×10^{-7} ; hydrogen peroxide, 5.7×10^{-2} ; carbonate buffer, 4.0×10^{-1} ; manganese(II) sulphate 1.0×10^{-8} (oxidation of azorubin S); pyrocatechol violet, 1.2×10^{-5} ; hydrogen peroxide, 3.9×10^{-2} ; borate buffer, 4.0×10^{-3} ; copper (II) sulphate, 1.6×10^{-8} (oxidation of pyrocatechol violet) and carminic acid, 2.4×10^{-6} ; hydrogen peroxide, 12.0×10^{-2} ; carbonate buffer, 1.2×10^{-5} (oxidation of carminic acid).

The absorbance of each solution was measured in a 1 cm^3 cell at 482 nm (oxidation of azorubin S), 500 nm (oxidation of pyrocatechol violet) and 523 nm (oxidation of carminic acid), every 30 s over a period of 3 min from the onset of the reaction.

RESULTS AND DISCUSSION

The effects of temperature and solvent concentration on the rates of the following reactions were investigated:

1. the oxidation of azorubin S by hydrogen peroxide, catalyzed by manganese(II), in the presence of carbonate buffer (pH 9.35),
2. the oxidation of pyrocatechol violet by hydrogen peroxide, catalyzed by copper(II), in the presence of borate buffer (pH 8.65), and
3. the oxidation of carminic acid by hydrogen peroxide, in the presence of carbonate buffer (pH 10), catalyzed by copper(II) and activated by methyl 5(2,4-dichlorophenoxy)-2-nitrobenzoate (bifenox).

Oxidation of azorubin S by hydrogen peroxide catalyzed by manganese(II)

On the basis of the results obtained in a previous paper,¹ the kinetic equation of this reaction was postulated as being:

$$-dc/dt = k [\text{H}_2\text{O}_2]^{0.4} [\text{buffer}] [\text{H}_3\text{O}^+] [\text{CH}_3\text{COCH}_3]^{0.5} [\text{Mn(II)}]$$

This equation is valid for hydrogen peroxide concentrations up to $5.7 \times 10^{-2} \text{ mol dm}^{-3}$, buffer concentrations ranging from 0.8×10^{-1} to $4.0 \times 10^{-1} \text{ mol dm}^{-3}$, H_3O^+ ions from 1.2×10^{-10} to $36 \times 10^{-10} \text{ mol dm}^{-3}$, acetone from 0.7 to 4.1 mol dm^{-3} and manganese(II) from 0.0 to $4.0 \times 10^{-6} \text{ mol dm}^{-3}$.

By following the reaction rate at different temperatures in the presence of various acetone concentrations, the corresponding rate constants, shown in Table I, were calculated. From this Table, it can be seen that with increasing temperature and acetone concentration up to 4.08 mol dm^{-3} , the rate constant of the reaction examined increases and at such an acetone concentration reaches its maximum. On the basis of these results it can be concluded that the catalytic effect of manganese(II) is most pronounced in the presence of 4.08 mol dm^{-3} of acetone.

TABLE I. The effect of temperature and acetone concentration on the oxidation of azorubin S by hydrogen peroxide, catalyzed by manganese(II)

T/K	$k \times 10^{-18} \text{ mol}^{-2.9} \text{ dm}^{8.7} \text{ s}^{-1}$			
	Acetone/ mol dm^{-3}			
	0	1.36	2.72	4.08
288.15	3.85	5.49	6.04	6.59
293.15	3.85	5.49	6.23	6.59
298.15	3.85	5.49	6.04	6.96
303.15	4.21	6.04	6.96	6.96

By means of this data, the kinetic parameters under the examined conditions were calculated in the usual way.⁵ The obtained results, shown in Table II, indicate that the enthalpy component (ΔH^\ddagger) of the Gibbs energy of activation, representing the energy needed to break old and form new chemical bonds in the transition state, as well as the entropy component (ΔS^\ddagger), exhibiting the change in the order of the system in the transition state, increase with increasing acetone concentration up to 4.08 mol dm^{-3} , at which concentration they reach their highest value. With further increase of the acetone concentration these values decrease. The change in the Gibbs energy of activation (ΔG^\ddagger) and the constant of the activated complex (pK^\ddagger) have their lowest value at 4.08 mol dm^{-3} of acetone, thus proving the largest effect of manganese(II) at such an acetone content.

TABLE II. The dependence of the kinetic parameters of the oxidation of azorubin S by hydrogen peroxide, catalyzed by manganese(II), on the acetone concentration ($T = 298.15 \text{ K}$)

Acetone/ mol dm^{-3}	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J K}^{-1} \text{ mol}^{-1}$	$-\Delta G^\ddagger/\text{kJ mol}^{-1}$	pK^\ddagger
1.36	3.07	124.33	33.90	5.79
2.72	3.63	126.67	34.14	5.99
4.08	8.63	144.62	34.49	6.05
5.44	6.96	137.86	34.14	5.98

Oxidation of pyrocatechol violet by hydrogen peroxide catalyzed by copper(II)

The kinetic equation of this reaction based on the results obtained in a previous paper¹ was formulated as being

$$-dc/dt = k [\text{H}_2\text{O}_2]^{-0.2} [\text{buffer}]^{-0.5} [\text{H}_3\text{O}^+] [\text{CH}_3\text{CN}]^{-0.3} [\text{Cu(II)}]$$

This equation is valid for the following reagent concentrations (mol dm^{-3}): hydrogen peroxide from 0.2×10^{-1} to 3.9×10^{-1} ; buffer from 0.4×10^{-2} to 2.4×10^{-2} ; H_3O^+ from 2.2×10^{-9} to 14×10^{-9} ; acetonitrile from 3.8 to 7.6 and copper(II) from 0.0 to 21×10^{-9} .

TABLE III. The effect of temperature and acetonitrile concentration on the oxidation of pyrocatechol violet by hydrogen peroxid, catalyzed by copper(II)

<i>T/K</i>	$k \times 10^{-10} \text{ mol}^{0.7} \text{ dm}^{-2.1} \text{ s}^{-1}$				
	Acetonitrile/ mol dm^{-3}				
	0	1.9	3.8	5.7	7.6
288.15	0.23	2.99	3.78	4.19	3.24
293.15	0.23	3.10	4.35	4.97	4.72
298.15	0.36	4.85	4.75	5.01	4.85

The calculated rate constants of this reaction at various temperatures and various acetonitrile concentrations are shown in Table III. From this Table it can be seen that the rate constant increases with increasing temperature and acetonitrile contents up to 5.7 mol dm^{-3} , at which point it reaches its maximum value, thus indicating that the catalytic effect of copper(II) is most pronounced at this concentration of acetonitrile. At higher acetonitrile contents the rate constant decreases.

TABLE IV. The dependence of the kinetic parameters of the oxidation of pyrocatechol violet by hydrogen peroxide, catalyzed by copper(II), on the acetonitrile concentration ($T = 293.15 \text{ K}$)

Acetonitrile/ mol dm^{-3}	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J K}^{-1} \text{ mol}^{-1}$	$\Delta G^\ddagger/\text{kJ mol}^{-1}$	$\text{p}K^\ddagger$
1.9	17.51	18.43	12.01	2.11
3.8	12.81	2.45	11.95	2.10
5.7	12.52	1.91	11.56	2.00
7.6	14.18	7.33	12.00	2.10

The effect of the acetonitrile concentration on the kinetic parameters of the reaction is shown in Table IV. The results in the Table show that the enthalpy (ΔH^\ddagger) and entropy (ΔS^\ddagger) decrease with increasing acetonitrile concentration, and that their lowest value is at 5.7 mol dm^{-3} , while at higher acetonitrile concentrations their values increase. The change of the Gibbs energy of activation (ΔG^\ddagger) and $\text{p}K^\ddagger$ reach their lowest values at 5.7 mol dm^{-3} of acetonitrile, thus proving that the catalytic effect of copper(II) is greatest at this concentration.

Oxidation of carminic acid by hydrogen peroxide catalyzed by copper(II) in the presence of bifenox

The kinetic equation of this reaction, postulated in a previous paper,² is found to be:

$$-dc/dt = k [\text{H}_2\text{O}_2] [\text{buffer}]^{-1} [\text{Cu(II)}] [\text{bifenox}] [\text{CH}_3\text{COCH}_3]^2 [\text{H}_3\text{O}^+]^{-0.4}$$

This equation is valid for hydrogen peroxide concentrations from 4.0×10^{-2} to $12.0 \times 10^{-2} \text{ mol dm}^{-3}$, buffer concentrations from 2.0×10^{-2} to $12.0 \times 10^{-2} \text{ mol dm}^{-3}$, copper(II) concentrations from 1.0×10^{-6} to $15.0 \times 10^{-6} \text{ mol dm}^{-3}$, acetone concentrations from 0.0 to $1.4 \times 10^{-1} \text{ mol dm}^{-3}$ and hydrogrn ion concentration from 3.2×10^{-11} to $1.4 \times 10^{-9} \text{ mol dm}^{-3}$.

The rate constants of this reaction, calculated on the basis of data obtained by measuring the reaction rate at various temperatures and vaious acetone concetrations are given in Table V. The results show that the rate constant increases with increasing temperature and acetone concentrations up to 0.14 mol dm^{-3} , at which concentration the maximum value is reached. The maximum reaction rate constant at 0.14 mol dm^{-3} acetone points to the strongest activation effect of bifenox under such conditions.

TABLE V. The effect of temperature and acetone concentration on the oxidation of carminic acid by hydrogen peroxide, catalyzed by copper(II) and activated by bifenox

T/K	$k \times 10^{-9} \text{ mol}^{2.5} \text{ dm}^{7.5} \text{ s}^{-1}$		
	Acetone/mol dm^{-3}		
	0.05	0.10	0.14
288.15	9.06	9.47	10.71
293.15	8.24	10.00	11.95
298.15	9.89	10.30	15.65
303.15	14.42	15.05	15.65

On the basis of the results obtained, the dependences of the kinetic parameters of the examined reaction on the solvent composition were established. The results obtained, given in Table VI, show that both the enthalpy (ΔH^\ddagger) and the entropy (ΔS^\ddagger) components of the free activations energy decrease with increasing acetone concentration up to 0.14 mol dm^{-3} , while with further increase in the acetone contents these values increase. From these data it can be seen that acetone effects both parameters wherby the effect on the entropy is greater.

The Gibbs energy of activation (ΔG^\ddagger) and pK^\ddagger reache their lowest values at 0.14 mol dm^{-3} acetone, thus proving that the activating effect of bifenox is most pronounced at this acetone concentration.

On the basis of all the above results it can be finally concluded that the presence of various organic solvents at various concentrations exhibit different effects both on the rate constants of the examined reactions and on the changes of the enthalpies,

entropies, free activation energies, and the constant of the activated complexes. In all instances the presence of the organic solvent effects both the enthalpy and entropy components of the free activation energy, in some cases effecting the entropy component more, which might be due partly to a change of the solvate sphere of the reagents and partly due to a change of the solvent structure at the point of the formation of the transition state.

TABLE VI. The dependence of the kinetic parameters of the oxidation of carminic acid by hydrogen peroxide, catalyzed by copper(II) and activated by bifenox, on the acetone concentration ($T = 298.15$ K)

Acetone/mol dm ⁻³	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J K}^{-1} \text{mol}^{-1}$	$\Delta G^\ddagger/\text{kJ mol}^{-1}$	pK^\ddagger
0.05	25.86	33.24	15.95	2.80
0.14	21.96	23.98	14.81	2.60
0.27	25.29	34.21	15.09	2.65
0.68	30.85	48.86	16.28	2.85

The obtained results are in accordance with our previous investigations.³

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ИЗВОД

ИСПИТИВАЊЕ УТИЦАЈА ОРГАНСКИХ РАСТВОРАЧА НА КИНЕТИЧКЕ ПАРАМЕТРЕ РЕАКЦИЈА КАТАЛИЗОВАНИХ МЕТАЛИМА

ЉИЉАНА ТРИФКОВИЋ и ГОРДАНА А. МИЛОВАНОВИЋ

Хемијски факултет, Универзитет у Београду, бр. 158, 11001 Београд

Испитан је утицај ацетона и ацетонитрила на кинетичке параметре оксидације ализарина С водоник-пероксидом, катализоване манганом(II), оксидације пирокатехин љубичастог водоник-пероксидом, катализоване бакром(II) и оксидације карминове киселине водоник-пероксидом, катализоване бакром(II) и активирани бифеноксом. Утврђено је да испитивани растварачи различито утичу на кинетичке параметре поменутих реакција. У свим случајевима концентрација растварача утиче како на енталпијски тако и на ентропијски удео слободне енергије при прелазу система у активно стање, као и на константу активираниог комплекса који при том настаје.

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