Thermochimica Acta, 125 (1988) 319–325
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

KINETIC–THERMOMETRIC STUDY OF HYDROGEN PEROXIDE DECOMPOSITION IN BASIC MEDIA CATALYZED BY Mn(II). INFLUENCE OF SEVERAL ORGANIC LIGANDS

M. CALULL, R. Ma. MARCÉ, P. RAMIREZ DE LA PISCINA, N. HOMS, J. TORRES and F. BORRULL

Departament de Química, Facultat de Ciències Químiques de Tarragona,
Universitat de Barcelona, 43005 Tarragona (Spain)

(Received 8 June 1987)

ABSTRACT

A kinetic–thermometric study of the influence of several organic ligands [hydrazine, tiron and triethylenetetramine (TETA)] in the hydrogen peroxide decomposition reaction catalyzed by Mn(II) in basic media is presented. All of these organic ligands form chelates with Mn(II).

The reaction rates were determined from the temperature–time curves. The limit of sensitivity obtained was 0.8 μg ml^{-1} for the reaction catalyzed by hydrazine–Mn(II) complex, 80 ng ml^{-1} for the reaction catalyzed by the tiron–Mn(II) complex and 0.1 ng ml^{-1} for the reaction catalyzed by the TETA–Mn(II) complex.

We have optimized this last reaction to determine Mn(II) based on the catalytic effect of the $[(\text{TETA})\text{-Mn(II)}-(\text{OH})]^+$ complex. The linear response range is for 0.1–13 ng ml^{-1} with a relative standard deviation of 2.5% for 4.5 ng ml^{-1} of Mn(II). It is known that a lot of metal ions catalyze this reaction, but only Fe(III) interferes at lower levels.

INTRODUCTION

The catalysis of the hydrogen peroxide decomposition by metal ions or their complexes in homogeneous systems has already been the subject of many investigations [1–3]. It is known that manganese catalyzes hydrogen peroxide decomposition in basic media. This catalytic effect is more active if other organic ligands are present in the reaction [4].

In the literature, kinetic–spectrophotometric methods have been applied to determine the catalytic activity of Mn(II) and the other metal ions (Co(II) [5], Cu(II) [6], Fe(III) [7], etc.) in the decomposition reaction of hydrogen peroxide in basic media, with different organic ligands. All these reactions offered possibilities for the development of a kinetic–thermometric method to determine traces of Mn(II).

A previous kinetic–thermometric study has been reported by Pantaler [8]. The effect of the Mn(II) complexes with aliphatic amines and heterocyclic bases on the reaction rate of decomposition of hydrogen peroxide in alkaline

0040-6031/88/$03.50

media has been studied thermometrically. The most active complex in this study was Mn(II)–1,10-phenanthroline. This method was applied to determine Mn(II) in alkali metal halides with a sensitivity of 5×10^{-6}%.

In previous papers, we established kinetic–thermometric methods, based on the hydrogen peroxide catalytic decomposition reaction, to determine traces of different metal ions with promising results (Cu(II) [9], Co(II) [10,11], Fe(III) [12]).

We report here a kinetic–thermometric study to determine the influence of the organic ligands hydrazine, tiron [pyrocatechol-3,5-disulfonic acid disodium salt (monohydrate)] and TETA (triethylenetetramine) in the hydrogen peroxide decomposition catalyzed by Mn(II). In this work we propose a new kinetic thermometric method to determine Mn(II) at ng ml^{-1} levels based on its catalytic action in the hydrogen peroxide decomposition using the most sensitive of the three systems studied ([TETA–Mn(II)–OH)$^{+}$]).

EXPERIMENTAL

Apparatus

The thermometric system, described elsewhere [9–12], comprises a nylon adiabatic cell, a rapid response thermistor of a thermometer type (with a nominal resistence of 100 kΩ at 25 °C), a Wheatstone bridge fed with 9.45 V from a stabilized source, a conventional stirrer, a recorder, and a 1-ml syringe for adding the catalyst or a solution for initiating the reaction. This temperature monitor is a modification of the apparatus of Lumbiarres et al. [13].

Reagents

Standard Mn(II) solution (1000 μg/ml) was obtained from Merck. More dilute solutions were prepared from this stock solution by dilution.

TETA 4.2% solution was prepared by dilution of concentrated triethylenetetramine R.A. (Fluka).

Hydrazine 24% solution was prepared by dilution of concentrated N_2H_5OH R.A. (Merck).

Tiron [pyrocatechol-3,5-disulfonic acid disodium salt (monohydrate)] Merck (art. 1922) was purified by precipitation in a water–ethanol mixture. A 0.0978 M solution was prepared and standardized.

A standard 0.974 M solution of NH_4OH was prepared by dilution of concentrated NH_4OH R.A. (Panreac).

A standard 23.87% (w/v) solution of H_2O_2 was prepared by dilution of H_2O_2 33% R.A. (Panreac).

The pH 10.5 buffer solution was $NaHCO_3$–NaOH.

Procedure

The procedure used was similar in all three cases. A known volume of the organic ligand, the appropriate quantity of Mn(II) solution, the buffer solution, and the required quantity of bidistilled water to a final volume of 80 ml are introduced into the cell. Once the mixture is thermally stabilized, a determined quantity of hydrogen peroxide (23%) is injected using the precision syringe and the thermometric curve is registered.

RESULTS

Examples of the three thermometric curves for each organic ligand are shown in Fig. 1, where the tan α value is obtained for a known quantity of catalyst in each case. In the experimental range the thermometric curves obtained in the TETA–Mn(II)–H_2O_2 and hydrazine–Mn(II)–H_2O_2 systems present good linearity and the slopes increase with Mn(II) concentration. The active species in the Mn(II)–TETA system in basic media for the catalytic decomposition of hydrogen peroxyde has been established [7] as the complex $[(TETA)\text{–}Mn(II)\text{–}(OH)]^+$. The thermometric curve of the tiron–Mn(II)–H_2O_2 system shows an induction time prior to a linear zone. This is probably due to the presence in the initial reaction of the inactive

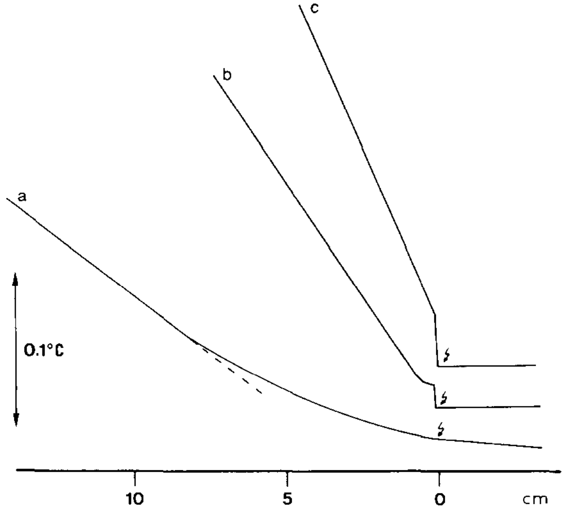

Fig. 1. Thermometric curves. (a) [Tiron] = 0.0121 M; [Mn(II)] = 61 ng ml^{-1}; addition of 0.5 ml of H_2O_2 23%. (b) [Hydrazine] = 0.2497 M; [Mn(II)] = 1.7 μg ml^{-1}; addition of 0.5 ml of H_2O_2 23%. (c) [TETA] = 0.26%; [Mn(II)] = 12.5 ng ml^{-1}; addition of 0.2 ml of H_2O_2 23%.

species MnT_3 under the experimental conditions [14,15], prior to the MnT_2 active complex. For this system, different alternative catalytic mechanisms with Mn(II) or Mn(III) complexes as intermediates of the reaction have been proposed [16–18].

We have optimized several variables in order to achieve maximum sensitivity and a wide range of application. Several assays were carried out with the aim of reaching the best reproducibility and precision. Since the organic ligand–hydrogen peroxide mixture reacts slowly, even in the absence of catalyst (probably due to the presence of impurities in the reagents), it was necessary to mix the organic ligand and the Mn(II) and when the mixture was thermally stabilized to introduce the hydrogen peroxide into the cell.

In order to achieve maximum reagent concentrations with minimum temperature increment of the blanks we performed several assays adding different organic ligand and hydrogen peroxide concentrations. The hydrogen peroxide concentration is limited by the injection volume, because an increase of injection volume produces a considerable distortion of the thermometric curve.

In the study of hydrazine–H_2O_2 and tiron–H_2O_2 in the absence of the catalyst, good linearity was obtained between tan α values and hydrazine concentrations, whereas this relationship is not so clear in the case of hydrogen peroxide.

In the TETA–H_2O_2 study good linearity was obtained between the tan α value and the concentration of NH_4OH; but non-linear relations between tan α and TETA and H_2O_2 concentrations were obtained.

A second study was made, on the influence of the pH value in the presence of catalyst in the reaction. In the case of hydrazine–H_2O_2 and tiron–H_2O_2, the maximum sensitivity was obtained at pH $\sim$ 10 (the pH was adjusted using the buffer solution), and in the other case, the pH is a function of the NH_4OH and TETA concentrations (under the conditions established the pH value is about 10–10.5). For all of them, maximum sensitivity was obtained about pH 10. At higher pH values the H_2O_2 may oxidize the Mn(II) speces to MnO_2. At lower pH values the Mn(II) complexes with different organic ligands [7,14] are not suitable complexes to catalyze the reaction.

Following these studies, we determined the optimum conditions for each case to determine Mn(II):

Hydrazine–H_2O_2: The optimum conditions in this case are 20 ml of 0.9988 M hydrazine, 40 ml of the pH = 10 buffer, an appropriate quantity of Mn(II), and bidistilled water to a final volume of 80 ml. Once thermal stability of the cell solution is achieved, hydrogen peroxide (23%) was added with a 0.5-ml syringe.

Tiron–H_2O_2: In this case we used 10 ml of the 0.0978 M tiron solution, the appropriate volume of Mn(II), 40 ml of buffer at pH 10.5, and the required quantity of bidistilled water to a final volume of 80 ml. The same quantity of hydrogen peroxide as was used for the hydrazine reaction was added.

TETA–H_2O_2: In order to achieve the best sensitivity, the following procedure is proposed: place 10 ml of 0.974 M NH_4OH, 5 ml of 4.2% TETA solution, the required volume of Mn(II), and bidistilled water to a final volume of 80 ml. In this case, only 0.2 ml of hydrogen peroxide was needed.

Using these conditions we have determined the range of linearity of the different methods and the sensitivity in each case: (a) with hydrazine the limit of sensitivity is 0.8 ppm, and the linearity range is 0.8–5 $\mu g\ ml^{-1}$; (b) with tiron the sensitivity is 80 ppb and the range of linearity is 80–250 ng ml^{-1}; (c) with TETA the sensitivity is 0.1 ppb, and the range of linearity is 0.1–13 ng ml^{-1}.

The different sensitivity values obtained with the different organic ligands studied may be related to the formation constants and coordinative unsaturation of the organic ligand–Mn(II) complexes.

INTERFERENCES

A study of the possible interferences was carried out. Different Mn(II) quantities (as a function of the organic ligand) were determined in the presence of a large number of ions: Hg(II), Ag(I), Pb(II), Cu(II), Cd(II), Bi(III), As(III), Sb(III), Sn(IV), Fe(II), Fe(III), Cr(III), Al(III), Zn(II), Ni(II), Co(II), Ca(II), Sr(II), Ba(II), Mg(II), Pd(II), Ti(IV), Mo(VI), U(VI), Au(III), Ce(IV), NO_3^-, Cl^-, and SO_4^{2-}. The Mn(II) determination was affected according to the organic ligand present: in the first case, hydrazine–H_2O_2, Co(II) and Cu(II) present a sensitivity limit higher than Mn(II), 2 ng ml^{-1}. Another important interfering species is Fe(III) with a sensitivity limit of 1 $\mu g\ ml^{-1}$; the rest of the metal ions interfere at greater concentrations (Pb(II) $>$ 20 $\mu g\ ml^{-1}$). The reaction catalyzed by Tiron–Mn(II) is more selective. In this case, only Co(II) at a concentration of 3 ng ml^{-1} interferes seriously; the rest of the metal ions interfere at greater concentrations (Ni(II) $>$ 3 ppm). The most sensitive and selective reaction is that catalyzed by $[(TETA)\text{–}Mn(II)\text{–}(OH)]^+$. The Mn(II) metal ion is the most sensitive, and only Fe(III) interferes at the 1.25 ng ml^{-1} level. The rest of the metal ions interfere at: Cu(II) $>$ 30, Co(II) $>$ 25, Ni(II) $>$ 50 $\mu g\ ml^{-1}$. In this last case, the interfering effect of iron is removed by its solvent extraction as the 1-(2-pyridylazo)-2-naphthorate complex.

CALIBRATION CURVE AND PRECISION

The calibration curve was obtained by preparing several solutions with different Mn(II) quantities. The application range of the method lies be-

TABLE 1

The analysis of unknown pure Mn(II) solutions

Mn(II) (ng ml^{-1})		Rel. error (%)
Added	Found [a]	
0.25	0.27 ± 0.03	8.0
0.90	0.94 ± 0.06	4.4
2.40	2.47 ± 0.10	2.91
6.3	6.50 ± 0.14	3.17
10.4	10.70 ± 0.20	2.88
12.6	12.83 ± 0.22	1.82

[a] Mean of three determinations.

tween (seven data points) 0.1 and 13 ng ml^{-1} of Mn(II) ($r = 0.9990$) with a relative standard deviation of 2.5% ($n = 7$) for 4.5 ng ml^{-1} of Mn(II) [$S = 50$ mV (0.02°C cm^{-1})].

Analyses of known manganese concentrations are summarized in Table 1.

CONCLUSIONS

We have determined by this kinetic–thermometric method the different catalytic activity of several Mn(II) complexes in the hydrogen peroxide decomposition reaction in basic media. This activity was proportional to the formation constants of these complexes. The more sensitive of these systems was that catalyzed by the $[(TETA)\text{–}Mn(II)\text{–}(OH)]^+$ complex. This method is selective to determine Mn(II) in the 0.1–13 ng ml^{-1} range, if the interference of Fe(III) is eliminated by extraction in organic solvent.

The low cost of the apparatus used, easy handling and the impossibility of poisoning the isolate transducer, make this technique very competitive with respect to traditional methods.

REFERENCES

1 N. Uri, Chem. Rev., 50 (1952) 375.
2 J.H. Baxendale, Advances in Catalysis and Related Subjects, Vol. 4, Academic Press, New York, 1952.
3 J.A. Connors and E.A.V. Ebsworth, Adv. Inorg. Chem. Radiochem., 6 (1964) 279.
4 Gmelins, Handbook of Inorganic Chemistry. MnD_3, Coordination Compounds, Springer-Verlag, 1982.
5 M. Otto and G. Werner, Anal. Chim. Acta, 147 (1983) 255.
6 H. Sigel, Angew. Chem. Int. Ed. Eng., 8 (1969) 167.
7 J.H. Wang, J. Am. Chem. Soc., 77 (1955) 4715.
8 R.P. Pantaler, L.D. Alfimova and A.M. Bulgakova, Zh. Anal. Khim., 30 (1975) 1584.

9 F. Borrull and V. Cerdà, Thermochim. Acta, 112 (1986) 335.
10 M. Calull, R.Ma. Marce, N. Homs, P. Ramirez de la Piscina and F. Borrull, Talanta (in press).
11 R.Ma. Marce, M. Calull, F. Borrull and V. Cerdà, Thermochim. Acta, 117 (1987) 89.
12 M. Calull, R.Ma. Marce, J. Torres and F. Borrull, The Analyst (in press).
13 J. Lumbiarres, C. Mongay and V. Cerdà, J. Therm. Anal., 22 (1981) 275.
14 M. Otto, H. Zwanziger and G. Werner, Inorg. Chim. Acta, 70 (1983) 41.
15 R. Genin and J.P. Scharff, Bull. Chem. Soc. Fr., 7–8 (1974) 1307.
16 A.E. Martell, Proceedings of the 3rd Symposium of Coordination Chemistry, Akademiai Kiado, Budapest, 1979.
17 C.A. Tyson and A.E. Martell, J. Am. Chem. Soc., 94 (1972) 939.
18 R.R. Grinstead, Biochemistry, 3 (1964) 1308.