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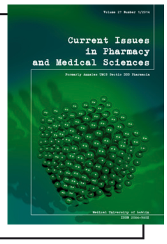


# Kinetics of the decomposition and the estimation of the stability of 10% aqueous and non-aqueous hydrogen peroxide solutions

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**ABSTRACT**

In this study, the stability of 10% hydrogen peroxide aqueous and non-aqueous solutions with the addition of 6% (w/w) of urea was evaluated. The solutions were stored at 20°C, 30°C and 40°C, and the decomposition of hydrogen peroxide proceeded according to first-order kinetics. With the addition of the urea in the solutions, the decomposition rate constant increased and the activation energy decreased. The temperature of storage also affected the decomposition of substance, however, 10% hydrogen peroxide solutions prepared in PEG-300, and stabilized with the addition of 6% (w/w) of urea had the best constancy.

## INTRODUCTION

Hydrogen peroxide is a chemically unstable substance, and it is usually used at the concentration of 30-35%. As a strong oxidant, it can react with other substances, resulting in decomposition. In concentrated solutions, stored at room temperature, however, the decomposition is slow. Diluted solutions of 3% hydrogen peroxide are used for disinfection and washing of wounds. More diluted solutions are used on the mucous membranes. The higher concentrations of hydrogen peroxide (6-10%, 30%) have various applications: as cautery agents, for disinfection of medical equipment, in cosmetology as whitening and oxidizing agents, in the chemical industry as a polymerizing agent and for the production of other preparations [1,2,4,9]. Mainly, these last are prepared as emulsions, powders and tablets [5,9]. Acetanilide, oxychinoline, tetrasodium pyrophosphate and several acids are used to obtain more stable preparations [2,5,8].

In current literature, stable complexes of hydrogen peroxide with many substances, i.a. Urea, are described [9]. Urea is an organic chemical compound, a diamide of carbonic acid. It forms colorless crystals of a melting point that is about 133°C. Moreover, it is hygroscopic, and is very soluble in water. Urea is used as a fertilizer and also as a reducer of catalytic reactions. In pharmacy, it is used as antibacterial and anti-protozoan agent. In cosmetology, it is used as a natural moisturizing factor (NMF), as in concentrations below 10%, it has a moisturizing effect. However, in concentrations above 10%, it has a peeling effect [12].

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The aim of this study was to examine the stability of 10% hydrogen peroxide solutions with or without the addition of urea, by accelerated aging methods at higher temperatures.

## MATERIALS AND METHODS

### Reagents

Hydrogen peroxide (30%), sulfate acid OD (98g/l), potassium permanganate (0.02 mol/l RM), glycerol (Poch.,Gliwice), polyethylene glycol 300 (LOBA – Chemie, Wien-Fischened PEG-300), 1,2- propanediol (Ph. Eur., Fuke Chemie PPG-1,2).

### Solutions preparation

Two series of solutions were prepared. The first series was that of 10% aqueous solutions of hydrogen peroxide with such solvents as water, polyethylene glycol 300 (PEG-300), 1,2-propanediol (PPG) and glycerol. The solutions were prepared by mixing hydrogen peroxide with these solvents. The second series of solutions had the addition of 6% urea (w/w). All solutions were then stored in amber glass bottles, in the dark, and at 20°C, 30°C or 40°C for 80 days.

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The composition of all solutions is given in Table 1.

***Table 1.*** Composition of the solutions

| Solution | Concentration of hydrogen peroxide (%) | Concentration of urea (%) | water (ml) | PPG-1,2 (ml) | PEG-300 (ml) | Glycerol (ml) |
|---|---|---|---|---|---|---|
| M0 | 10 | - | 90 | - | - | - |
| M6 | 10 | 6 | 84 | - | - | - |
| M PPG | 10 | - | - | 90 | - | - |
| M6 PPG | 10 | 6 | - | 84 | - | - |
| M PEG | 10 | - | - | - | 90 | - |
| M6 PEG | 10 | 6 | - | - | 84 | - |
| M G | 10 | - | - | - | - | 90 |
| M6 G | 10 | 6 | - | - | - | 84 |

## Methods

### Determination of 10% $H_2O_2$ solutions:

Determination of hydrogen peroxide content in the solutions was according to FP IX [7]. Each time, 1 g of the solution was weighed and subsequently diluted with 27 ml of water (solution 1). Then, 7 ml of this solution was taken and 14 ml of sulfate acid (98 g/l) OD was added (solution 2).

Solution 2 was titrated with $KMnO_4$ (0.02 mol/l) until a pink color was evident.

1 ml $KMnO_4$ corresponds to 1.7 mg $H_2O_2$.

The content of $H_2O_2$ was calculated by the following equation:

$$x\% = v \cdot 1.7 \cdot 100/1000 = 0.17 \cdot 4 \cdot V$$

x% – the concentration (%) of hydrogen peroxide in the sample
1.7/1000 – the amount (mg) of hydrogen peroxide per 1 ml of $KMnO_4$
4-100 – dilution of the solution
V – the amount (ml) of KMnO4

## RESULTS

The stability of hydrogen peroxide was examined in aqueous and non-aqueous solutions, with 6% of urea or without urea. The aqueous solutions were stored at 20°C-40°C (Fig. 1-3). In the time allotted to the experiment, at 20°C, the decrease of the concentration of hydrogen peroxide in the solutions without urea was 2.16%, and in the solutions with the addition of urea this was 60.7% (Fig. 1). At 30°C, in the solutions without the addition of urea, and with 6% of urea, a decrease in the concentration of, respectively, 12.3% and 53.5% was observed (Fig. 2). In the solutions without urea stored at 40°C (Fig. 3), the decrease of hydrogen peroxide concentration was 73.5%, but in the solutions with urea, full decomposition occurred after only a few days. In the solutions with 1, 2-propanediol (PPG-1,2) and glycerol as the solvents, the full decomposition of hydrogen peroxide was observed immediately after the preparation. In the solutions with polyethylene glycol 300 as the solvent, and with the addition of 6% of urea (Fig. 4), the decrease of hydrogen peroxide content was about 1% (at 20°C) and 2.5% (at 30°C).

### Kinetics of the decomposition

The content of hydrogen peroxide versus time of storage is shown in the supplied figures as lnC = f (t). The analysis of the hydrogen peroxide content (average of 3 measurements) is illustrated in Fig. 1-4. The standard deviations of the series of determinations were not different significantly, and were SD±0.002-0.026.

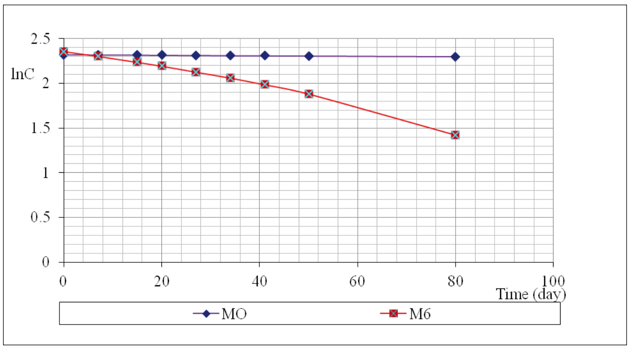



***Figure 1.*** Effect of storage time at 20°C on the concentrations of hydrogen peroxide in 10% aqueous solutions with and without urea

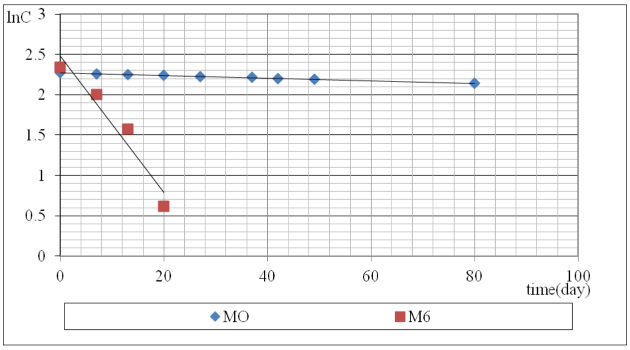



***Figure 2.*** Effect of storage time at 30°C on the concentrations of hydrogen peroxide in 10% aqueous solutions with and without urea

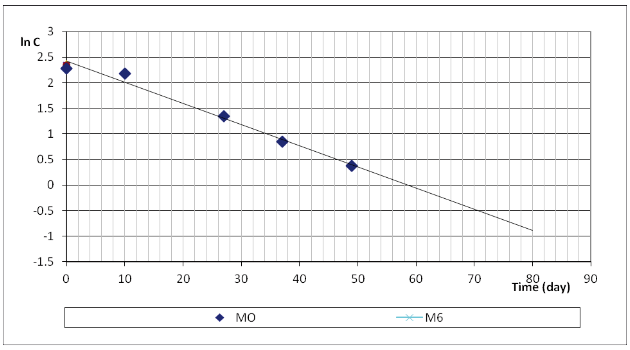



***Figure 3.*** Effect of storage time at 40°C on the concentrations of hydrogen peroxide in 10% aqueous solutions with and without urea

MO – aqueous solution of 10% hydrogen peroxide without urea,
M6 – aqueous solution of 10% hydrogen peroxide with 6% addition of urea.

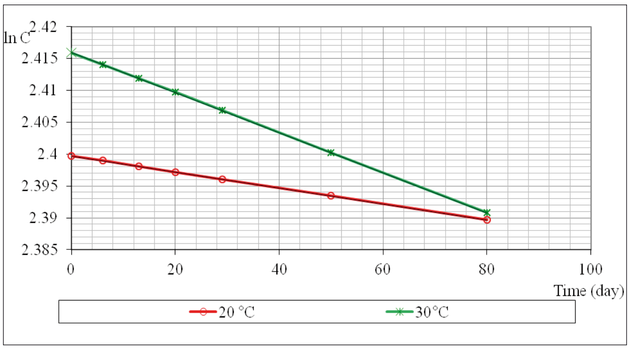
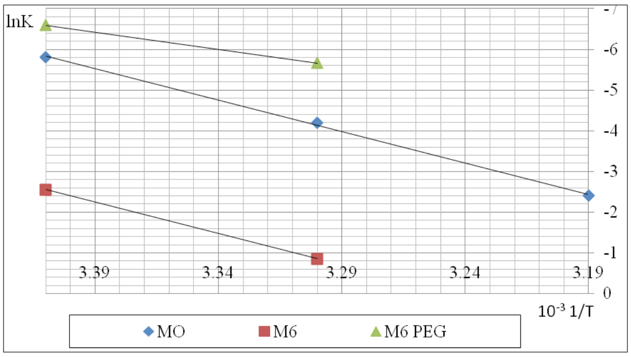



***Figure 4.*** Effect of storage time at 20 and 30°C on the concentrations of hydrogen peroxide in 10% non-aqueous solutions (PEG-300) with 6% urea

Next, the decomposition rate constants (K) of the hydrogen peroxide solutions were calculated. The linear graphs of K versus absolute temperature (1/T) are presented in Fig. 5.




MO – aqueous solution of 10% hydrogen peroxide without urea,
M6 – aqueous solution of 10% hydrogen peroxide with 6% addition of urea,
M6-PEG – solution of 10% hydrogen peroxide with PEG and 6% urea

***Figure 5.*** The relationship between decomposition rate constants of hydrogen peroxide and temperature of storage

Based on the decomposition rate constants, Arrhenius's equation [3,11] and obtained results, the activation energy at room temperature was calculated.

$$Ea = \frac{\ln K_1 - \ln K_2}{T_2 - T_1} \cdot 1.9872 \cdot T_2 \cdot T_1$$

$$\ln K_{20} = \ln K_2 \cdot \frac{E\,(T_2 - T_{20})}{1.9872 \cdot T_2 \cdot T_{20}}$$

$K_1 > K_2$, $T_2 > T_1$, $T_2 > T_{20}$
1.9872 – the gas constant
$K_{20}$ – the decomposition rate constant at 20°C
$T_{20}$ – the room temperature
$K_1$, $K_2$ – the determined decomposition rate constants

The stability of hydrogen peroxide ($t_{10\%}$) in the solutions stored at 20°C was calculated by the equation:

$$t_{10\%} = \frac{0.1053}{K_{20}}$$

$t_{10\%}$- the disintegration time of 10% active substance
$K_{20}$ – the decomposition rate constant at 20°C

The results of K calculated, Ea and $t_{10\%}$ are given in Table 2.

***Table 2.*** Kinetics of the hydrogen peroxide decomposition in 10% solutions

| Solution | $K_{exp.}$ (day$^{-1}$) Temperature (°C) | | | Ea (cal·mol$^{-1}$) | $K_{cal}$ (day$^{-1}$) at 20°C | $t_{10\%}$ at 20°C (day) | |
|---|---|---|---|---|---|---|---|
| | 20°C | 30°C | 40°C | | | experimental | calculated |
| M0 | $3.01 \cdot 10^{-3}$ | $1.5 \cdot 10^{-2}$ | $9.0 \cdot 10^{-2}$ | 31051.77 | $2.58 \cdot 10^{-3}$ | 35.1 | 40.81 |
| M6 | $7.8 \cdot 10^{-2}$ | $4.26 \cdot 10^{-1}$ | - | 29938.77 | $7.8 \cdot 10^{-2}$ | 1.35 | 1.35 |
| M6 PEG | $1.37 \cdot 10^{-3}$ | $3.47 \cdot 10^{-3}$ | - | 16354.28 | $1.38 \cdot 10^{-3}$ | 76.86 | 76.3 |

$K_{exp}$ – experimental decomposition rate constants; Ea – Activation energy ; $K_{cal}$ – calculated decomposition rate constants; $t_{10\%}$ – decomposition time of 10% active substance

## DISCUSSION

Hydrogen peroxide is a very commonly used substance in the pharmaceutical industry. Because of its quite rapid decomposition, substances which enhance the stability are added. In the literature, preparations of complexes of hydrogen peroxide and peroxyfluorohafnate, calcium dioxide, sodium pyrophosphate, potassium bicarbonate, barium fluoride hydroperoxide, ammonium fluoride hydroperoxide and urea, are described [5,6,9,13]. These are produced in solid forms, as powders, granules and capsules. Hydrogen peroxide as a solid compound, containing about 35% of hydrogen peroxide, is called "urea peroxide". This, diluted in glycerol anhydrous and stabilized with 8-hydroxychinoline, is used in infection treatments. In medicine, hydrogen peroxide is usually used as aqueous solutions, although, sometimes, non-aqueous solutions with isopropanol, glycerol anhydrous, propylene glycol or polyoxyethyleneglycol are also prepared. Until our work was done, there was little data on the stability of varied percentages of hydrogen peroxide within these aqueous and non-aqueous solvents. In previous work, the stability effects on aqueous and non-aqueous 3% solutions of hydrogen peroxide with the addition of 2%-10% urea were determined [14]. In this research, it was found that the addition of the urea has no effect on the stability of the aqueous solutions. Moreover, the decomposition of hydrogen peroxide increased with temperature. However, a solution with PEG-300 and 6% (w/w) of urea was considered stable.

In our study, the stability of 10% solutions of hydrogen peroxide with the addition of 6% (w/w) urea was examined. It was discovered the urea is a better stabilizer in the 10% solutions stored at 20°C than it is with 3% solutions, but the effect is not strong. We also ascertained that an increase of temperature of the storage of the 10% hydrogen peroxide solutions without urea induced a faster decomposition of the substance. This effect is evidenced by the calculated decomposition rate constants K ($K_{20°C}=3.0 \cdot 10^{-3}$ d$^{-1}$, $K_{30°C}=1,5 \cdot 10^{-2}$ d$^{-1}$, $K_{40°C}=9.0 \cdot 10^{-2}$ d$^{-1}$). In the solutions stabilized with the addition of urea, the decomposition rate constants were higher ($K_{20°C}=7.8 \cdot 10^{-2}$ d$^{-1}$ and $K_{30°C}= 4.26 \cdot 10^{-1}$ d$^{-1}$).

At 40°C, the decomposition of hydrogen peroxide with or without urea, was complete.

The activation energy ($E_a$) of aqueous solutions without urea was 31051.77 cal·mol$^{-1}$. Of solutions stabilized with urea, this figure was 29938.77 cal·mol$^{-1}$. The next criterion of stability was evaluation of the decomposition of 10% hydrogen peroxide at room temperature. Time $t_{10\%}$, as dependent on the employment of the decomposition constant (K calculated and K determined) at 20°C, was, respectively, 35.1 days and 40.8 days.

Our work shows that non-aqueous solvents: PPG-1,2 and glycerol cannot be used for the preparation of hydrogen peroxide solutions. The full decomposition of these solutions, whether stabilized and not stabilized with urea, followed immediately after preparation. However, solutions stabilized with 6% (w/w) of urea in PEG-300 and stored at 20°C or 30°C were more stable than analogous aqueous solutions. Because of the better stability, the non-aqueous solutions of hydrogen peroxide can be used as skin disinfectants and antiseptic agents.

## CONCLUSIONS

1. In 10% solutions stored at 20°C-40°C, the decomposition of hydrogen peroxide proceeds according to first-order kinetics.
2. The addition of 6% (w/w) of urea to aqueous solutions of hydrogen peroxide does not bring about an increase in their stability.
3. Non-aqueous solutions prepared in PPG-1,2 and glycerol, with the addition of 6% (w/w) of urea decompose immediately after preparation.
4. Solutions of 10% of hydrogen peroxide with the addition of 6% (w/w) of urea prepared in PEG-300, are more stable than aqueous solutions.
5. The activation energy required for decomposition of the substance, in the aqueous solutions is slightly higher than in non-aqueous solutions and solutions stabilized with urea.

## REFERENCES

1. Ahmad S.I.: Control of skin infections by a combined action of ultraviolet A (from sun or UVA lamp) and hydrogen peroxide (HUVA therapy), with special emphasis on leprosy. *Med Hypotheses*. 4, 484-6, 2001.
2. Alfa M.J., Jackson M.: A new hydrogen peroxide based medical device detergent with germicidal properties: composition with enzymatic cleaners. *Am. J. Infect. Control*. 29, 168, 2001.
3. Bauer K.H. et al.: (2012). Techonologia postaci leku z elementami biofarmacji. MedPharm Polska.
4. Bittencourt Berge S., et al.: Changes in the stiffness of demineralized dentin following application of tooth whitening agents. *Acta Odonto. Scand*., 70, 56-60, 2012.
5. Bradecka B., Krystek A.: Preparation of stable sodium percarbonate, an ecologically safe bleach. *Przem. Chem*. 70, 430, 1991.
6. Dobado J.A., Molina J., Portal D.: Theoretical Study on the Urea-Hydrogen Peroxide 1:1 Complexes. *J. Phys. Chem*. A. 102(4), 778-784, 1998.
7. Farmakopea Polska wydanie IX (2011). Minister Zdrowia, Urząd Rejestracji Produktów Leczniczych, Wyrobów Medycznych i Produktów Biobójczych, Warszawa.
8. Laat J., Gallard H.: Catalytic Decomposition of Hydrogen Peroxide by Fe(III) in Homogeneous Aqueous Solution: Mechanism and Kinetic Modeling. *Environ. Sci. Technol*. 33, 2726-2732, 1999.
9. Login R.B. et al.: Stabilization of disinfectant urea-hydrogen peroxide complexes with PVP. US 5,183,901 (Cl. 548-543; C01B15/01), 02 Feb 1993, *Appl*. 825,359, 24 Jan 1992.
10. López-Lázaro M.: Dual role of hydrogen peroxide in cancer: possible relevance to cancer chemoprevention and therapy. *Cancer Lett*. 8, 1-8, 2007.
11. Militký J., Čáp J.: Improved parameter estimation in arrhenius type models. *Thermochim Acta*. 92, 77-80, 1985.
12. Molski M.: Chemia piękna. Polskie Wydawnictwo Naukowe, Warszawa, 2012.
13. Siddiquii S., et al.: A study of hydrogen peroxide decomposition in ammonia-peroxide mixtures (APM). *Micro. Eng*., 103, 68-73, 2013.
14. Zuń M., et al.: Influence of concentration of the urea on the hydrogen peroxide content in 3% aqueous and non-aqueous solutions stored at different temperatures. *Ann UMCS Sect DDD. 2*, 47-55, 2011.