

Contributions to the Reaction Mechanism of Photochemical Decomposition of Hydrogen Peroxide in Aqueous Solution

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The present paper brings new contributions to the elucidation of indirect degenerated branching mechanism of the photochemical decomposition of hydrogen peroxide (30%) in aqueous solution. By using an isobar-isothermal equipment for measuring the volume of oxygen evolved by hydrogen peroxide decomposition in the presence of IR, Vis, UV radiations and on the basis of the theoretical laws advanced by N.N. Semenov for the indirect degenerated branching reactions the following amounts were calculated: the branching factor, ϕ , the initiation rate v_i and the induction period, τ , for the three cases. The values resulted for the branching factor, ϕ , agree with its range of variation for the indirect degenerated branching reactions which supports the advanced mechanism bringing a contribution to the development of the chain reactions field.

Keywords: 30% hydrogen peroxide, photochemical decomposition, mechanism, branching factor, ϕ , initiation rate, v_i , induction period, τ .

In order to extend our previous studies on the kinetics and mechanism of the indirect degenerated branching reactions [1-6] the present paper brings new contributions to the reaction mechanism of photochemical decomposition of hydrogen peroxide (30%) in aqueous solution whose mechanism belongs to this field [7].

The hydrogen peroxide is known as a liquid substance, thermally stable under cold conditions and in the absence of impurities but suffering a strongly exothermal decomposition into water and oxygen when heated: [8, 9].



The thermal decomposition reaction was found experimentally to proceed violently or even with explosion with hydrogen peroxide in pure state or as a concentrated solution

The H_2O_2 decomposition is catalyzed by alkali even when diluted such as those released by the common glass. This is why the hydrogen peroxide with no stabilizers (phosphoric acid, sodium diphosphate etc) is usually preserved in polyethylene bottles or in bottles covered by a paraffin layer, in dark, at low temperature (6-7°C).

The thermal decomposition of hydrogen peroxide is also promoted by nonspecific heterogeneous catalysts as rough surfaces, the impurities in the vessels (dust), by specific catalysts such as MnO_2 , Hg, Pd/SiO₂ [10] or some enzymes (catalase) [8].

Many complex reactions with formation of hydrogen peroxide were found to proceed through the free radicals (HO_2 , OH) as chain reactions [11].

The above mentioned experimental findings made evident the H_2O_2 decomposition under certain conditions to proceed probably by a branched chain radicalic reaction showing the characteristics of this mechanism [2-4].

The studied reported by Rabitz and co-workers [12] regarding the thermal decomposition of H_2O_2 (750 K, $p_{O_{H_2O_2}} = 213$ torr, $p_{Ar} = 360$ torr) made evident the reaction

to proceed as a branched chain reaction. The mechanism advanced on the basis of experimental data was confirmed theoretically by sensitivity analysis [13, 14].

The H_2O_2 decomposition in solution can develop in the presence of the catalysts: -transitional metallic ions (Fe^{3+} , Fe^{2+} , Ca^{2+}), coordinative compounds or anionic catalysts (MoO_4^{2-} , CrO_4^{2-} , WO_4^{2-}), the reactions being placed in the category of homogeneous catalytic reactions in solution [15].

The H_2O_2 decomposition in aqueous solution is a photochemical reaction [16] since H_2O_2 is a photochemically active species ($\lambda(\text{Å}) = 2750-3660$).

The quantum yield, η , lies between 20-500 so that the photochemical decomposition of aqueous hydrogen peroxide belongs to the category of photochemical reactions with $\eta \gg 1$ which can proceed by only a chain mechanism similar to the reactions of HCl formation ($\eta = 10^4-10^6$), chlorination of CH_4 ($\eta \approx 10^4$), formation of $COCl_2$ ($\eta \approx 10^3$) and chlorination of benzene ($\eta \approx 600$) [7,16].

The mechanism advanced for the photochemical decomposition of aqueous H_2O_2 is an indirect branched [7] chain as shown in figure 1.

As revealed in figure 1 the H_2O_4 is the relatively stable intermediate responsible for the indirect branching of the chain and the branching reaction is similar to that of photochemical initiation.

The present paper is aimed to evaluate the branching factor, ϕ , the initiation reaction, v_i , and the induction period τ in the presence of IR, Vis and UV radiations based on the theoretical law of the branched chain reactions [17,18].

The value of the obtained branching factor situated between 0.076-0.183 min^{-1} for the H_2O_2 decomposition in the presence of IR, Vis, UV radiations lies within the variation domain of ϕ for this type of indirect branched chain reaction (0.01-1 min^{-1}) [6].

The obtained results support this mechanism for the photochemical decomposition of aqueous H_2O_2 (30%)

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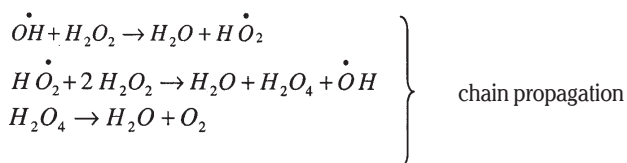


Fig. 1. Indirect degraded branching reaction mechanism of photochemical decomposition of H_2O_2

(perhydrol), this solution being usually used in various purposes (oxidizer, decolourant, disinfectant as antiseptic, etc.).

Experimental part

Equipment and working procedure

The isotherm-isobar installation used for the study on photochemical decomposition of hydrogen peroxide (30%) by the volumetric method is presented in figure 2.

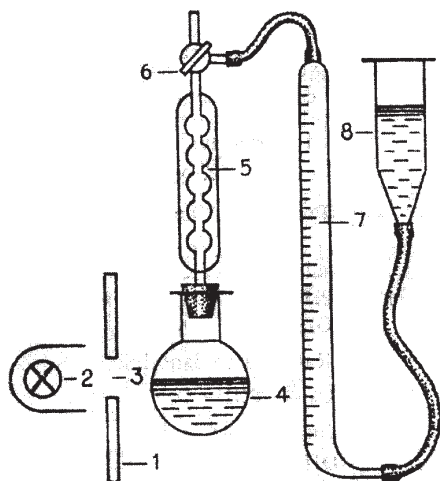


Fig. 2. Installation used for the study of photochemical decomposition of H_2O_2 (30%) by the volumetric method. 1.-protective screen; 2.-mercury lamp; 3.-slot; 4.-quartz flask of 50-100 cm^3 ; 5.-cooler 6.-two-way tap; 7.-graduated burette; 8.-communicating vessels [7]

Working procedure

30 mL of 30% H_2O_2 are placed into the quartz flask (4) and three experiments are then performed successively and the data reproducibility checked every time.

The first experiment was run in the dark (IR radiations) with the quartz flask isolated from light, the second under the influence of the daylight (radiations in the visible region) and the third under the action of ultraviolet radiations when the mercury lamp 2 (fig.2) is putting into service, the working procedure being the same.

The gas volume (O_2) was measured every 3 min. after the reaction onset for the reaction in dark, (IR) 2 min. for the reaction at the daylight (Vis) and 1 min. for the reaction under the action of the ultraviolet radiations (UV). The time intervals were thus settled as to have enough experimental runs for estimating the branching factor. The experiments were made at constant temperature and pressure, 25°C, 760 mm Hg.

The Merck starting H_2O_2 solution was used and 30% solution (by vol.) prepared.

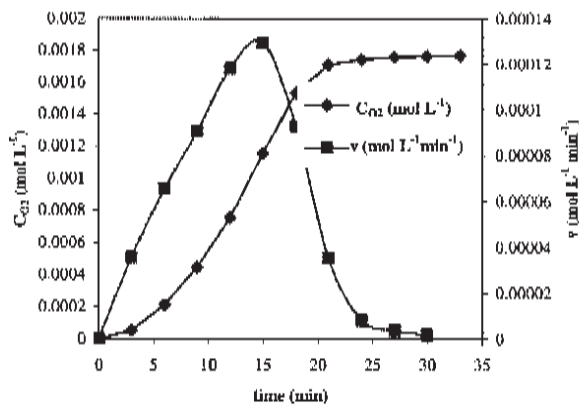
Results and discussion

In table 1 the experimental data obtained by photochemical decomposition of H_2O_2 (30%) in the presence of IR, Vis, UV radiations are presented, namely the oxygen volume V_{O_2} (cm^3) at different times as well as the corresponding oxygen concentration, C_{O_2} (mol/L).

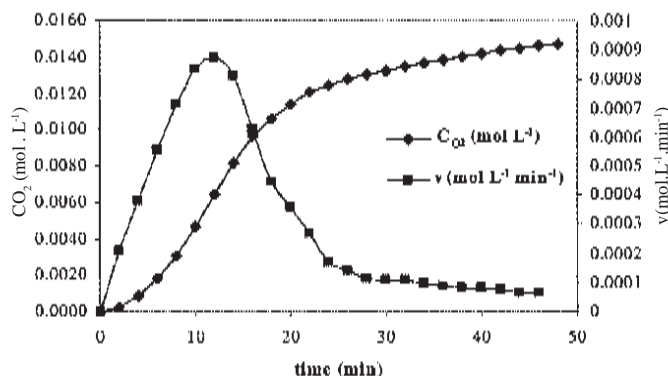
Based on data in table 1 the kinetic curves C_{O_2} -time are depicted in figure 3 a,b,c along with the curves representing the formation rate of oxygen obtained by the numerical differentiation of the kinetic curves.

Table 1
EXPERIMENTAL (VO_2) AND PROCESSED (CO_2) DATA OBTAINED WITH THE PHOTOCHEMICAL DECOMPOSITION OF H_2O_2 (30%) IN THE PRESENCE OF IR, Vis, UV RADIATIONS.

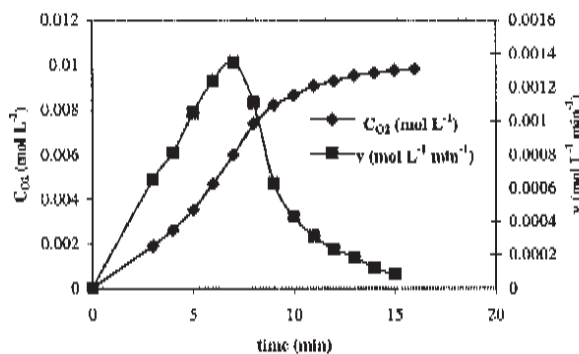
IR	t (min)	0	3	6	9	12	15	18	21	24	27	30	33	36		
	V_{O_2} (cm^3)	0	0.04	0.16	0.33	0.55	0.84	1.12	1.23	1.28	1.29	1.30	1.31	1.31		
	C_{O_2} ($mol \cdot L^{-1}$) $\cdot 10^{-3}$	0	0.055	0.213	0.447	0.756	1.155	1.533	1.711	1.744	1.760	1.766	1.772	1.772		
Vis	t (min)	0	2	4	6	8	10	12	14	16	18	20	22	24		
	V_{O_2} (cm^3)	0	0.22	0.62	0.94	1.57	2.40	3.28	4.18	4.94	5.46	5.84	6.19	6.39		
	C_{O_2} ($mol \cdot L^{-1}$) $\cdot 10^{-3}$	0	0.300	0.840	1.820	3.050	4.680	6.400	8.170	9.650	10.68	11.42	12.11	12.50		
	t (min)		26	28	30	32	34	36	38	40	42	44	46	48		
	V_{O_2} (cm^3)		6.54	6.68	6.78	6.90	7.00	7.10	7.18	7.26	7.34	7.42	7.48	7.56		
C_{O_2} ($mol \cdot L^{-1}$) $\cdot 10^{-3}$		12.80	13.07	13.27	13.50	13.70	13.90	14.06	14.22	14.38	14.53	14.65	14.80			
UV	t (min)	0	3	4	5	6	7	8	9	10	11	12	13	14	15	16
	V_{O_2} (cm^3)	0	0.46	0.63	0.85	1.13	1.44	1.78	1.98	2.09	2.19	2.24	2.30	2.33	2.36	2.37
	C_{O_2} ($mol \cdot L^{-1}$) $\cdot 10^{-3}$	0	1.890	2.600	3.520	4.700	6.000	7.400	8.220	8.660	9.070	9.280	9.530	9.650	9.770	9.810



a- IR;



b- Vis



c- UV

Fig. 3.a,b,c: Kinetic curves C_{O_2} -time and v -time for the photochemical decomposition of H_2O_2 (30%) a-IR; b- Vis; c-UV

The kinetic curves are seen to be of the S shape [6] and have a clear inflexion point that coincides with the maximum rate of O_2 formation. These kinetic characteristics are specific to the indirect degenerated branching reactions [6, 18].

In this case, the indirect branching with the preponderant formation of O_2 is dependent on the formation of a molecular and rather stable intermediate (H_2O_4) that can lead to branching only after its accumulation in a critical (maximum) concentration in the main chain.

It was found experimentally that with the indirect degenerated branching reactions the inflexion point on the kinetic curve and the maximum rate of the final product formation, respectively, correspond to the maximum concentration of the molecular intermediate product responsible for branching, this behavior being also confirmed by the kinetic theory of the mechanism of such a type [17-19].

Starting from the definition of the induction period [20] as the time necessary for the final product formation rate to attain the maximum value and the same about the concentration of the molecular intermediate it can be noticed in figure 3a-c that the induction periods are the following with the three cases under study:

$$\lambda_{IR} = 15 \text{ min}; \quad \lambda_{Vis} = 12 \text{ min}; \quad \lambda_{UV} = 7 \text{ min};$$

The fact is made evident in figure 4 that the induction period decreases with increasing energy associated to the respective radiations as it was expected. Thus, since the branching is photochemical it would lead in a shorter time to oxygen formation when the energy associated to the radiation is higher, e.g. 10^2 - 10^4 KJ/mol at the UV necessary for splitting the chemical bond in H_2O_4 resulting in formation of $2OH + O_2$ (~146 KJ/mol) and consequently the maximum formation rate of O_2 is attained in a shorter time.

The branching factor ϕ also referred to as the global branching factor represents the difference between the frequencies of the branching propagation reactions and of the interruption ones and it is involved in the Simenov law for indirect degenerated branching reactions of the following form [17]:

$$v = A \cdot e^{\phi t} \quad (1)$$

where

v - reaction rate (mol L⁻¹ min⁻¹);

A - a constant at the constant temperature (mol L⁻¹);

ϕ - branching factor (min⁻¹);

t - time (min).

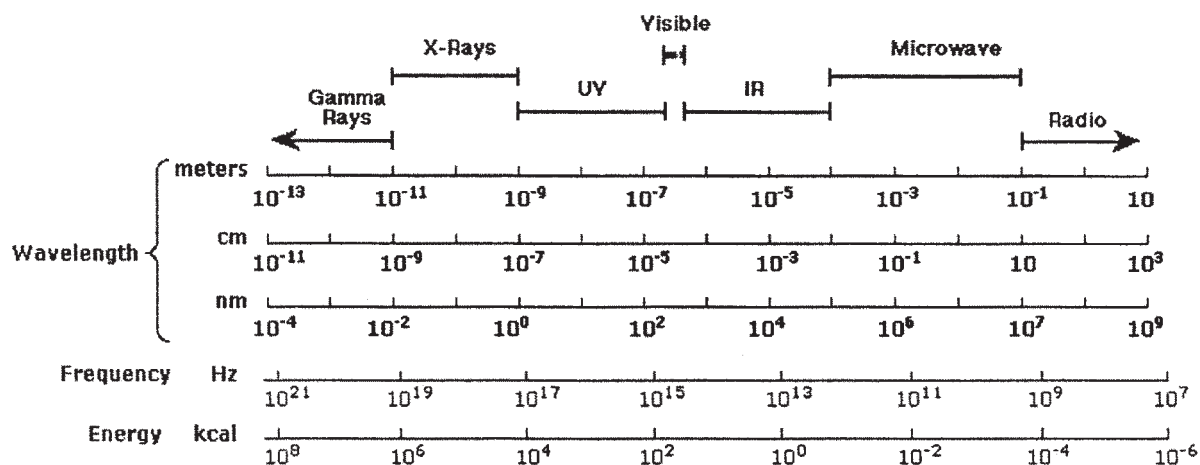


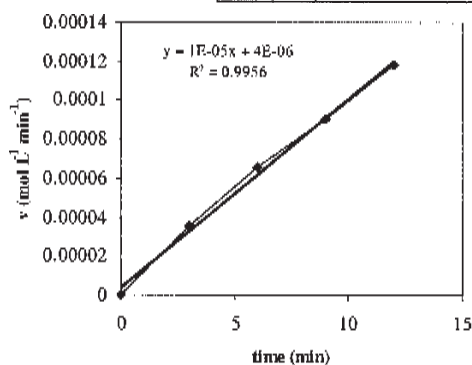
Fig. 4. The Electromagnetic Spectrum

IR	t (min)	0	3	6	9	12	15	
	C _{O2} (mol·L ⁻¹)·10 ⁻³	0	0.055	0.213	0.447	0.756	1.155	
	v	0	0.0000355	0.0000653	0.0000905	0.0001180	0.0000630	
	ln(v)		-10.24598	-9.636008	-9.310161	-9.044826	-9.672376	
Vis	t (min)	0	2	4	6	8	10	12
	C _{O2} (mol·L ⁻¹)·10 ⁻²	0	0.03	0.084	0.182	0.305	0.468	0.64
	v	0	0.00021	0.00038	0.000553	0.000715	0.000838	0.000468
	ln(v)		-8.468403	-7.875339	-7.501057	-7.243228	-7.085089	-7.66704
UV	t (min)	0	3	4	5	6	7	
	C _{O2} (mol·L ⁻¹)·10 ⁻³	0	1.89	2.6	3.52	4.7	6	
	v	0	0.00065	0.000815	0.00105	0.00124	0.000783	
	ln(v)		-7.338538	-7.112322	-6.858965	-6.692644	-7.151952	

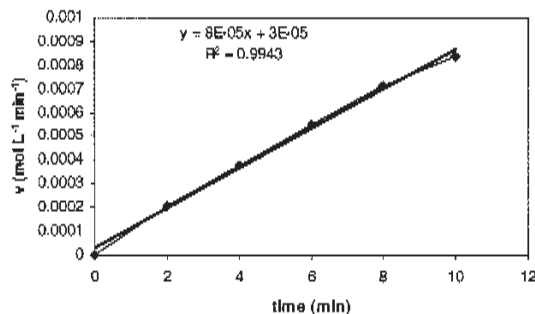
Table 2
EXPERIMENTAL AND
PROCESSED DATA FOR
ESTIMATING THE FACTOR ϕ
AND THE CONSTANT A

Table 3
VALUES OF INDUCTION PERIOD, τ , BRANCHING FACTOR, ϕ , AND INITIATION RATE, v_i , OBTAINED
WITH THE PHOTOCHEMICAL DECOMPOSITION OF H₂O₂ (IR, Vis, UV)

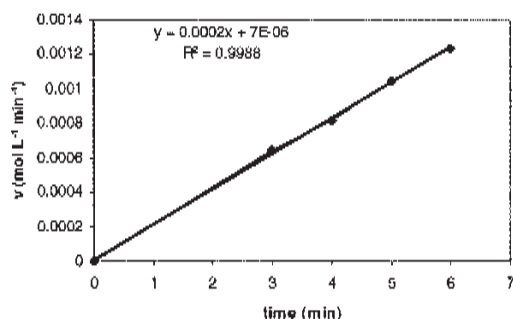
	τ (min)	ϕ (min ⁻¹)	A (mol L ⁻¹) 10 ⁴	v_i (mol L ⁻¹ min ⁻¹) 10 ⁴
IR	15	0.076	0.314	0.0239
Vis	12	0.104	3.226	0.3351
UV	7	0.183	4.568	0.8347



a- IR



b- Vis



c-UV

Fig. 5.a,b,c: Graphic representation of equation (3)
a- IR; b- Vis; c-UV

This relationship holds till the inflexion point is attained on the corresponding kinetic curve up to the maximum reaction rate value [6, 17, 21].

For the reaction under study the equation (1) becomes:

$$v_{O_2} = \frac{d[O_2]}{dt} = A \cdot e^{\phi t} \quad (2)$$

The linearization of the equation (2) gives the relationship:

$$\ln v_{O_2} = \ln A + \phi t \quad (3)$$

It follows that the relationships 3 derived on the basis of the indirect degenerated branching reactions theory is the basis of the estimation of the branching factor ϕ and of the initiation rate v_i [6] since

$$A \cong \frac{v_i}{\phi} \quad (4)$$

on the basis of experimental data for the three cases.

The table 2 includes the experimental and processed data necessary for drawing the straight lines according to the equation 3 for estimating the branching factor ϕ and the constant A (relationship 4).

The equation (3) is plotted in fig. 3a-c which gives the values of the branching factor ϕ for the three cases.

The table 3 presents the values obtained for ϕ , λ and v_i for the photochemical decomposition of H₂O₂ under the action of IR, Vis, UV radiations where ϕ and v_i are seen to increase with increasing energy associated to the radiations which confirms that the initiation and branching reactions are photochemical (fig. 1).

The resulting value of the branching factor between 0.076-0.183 min⁻¹ for the photochemical decomposition of the H₂O₂ (30%) is placed within the variation domain of ϕ for the indirect degenerated branching reactions, of 0.01-1 min⁻¹ [19].

These results are in favor of the indirect degenerated branching mechanism for the photochemical decomposition of H₂O₂ (30%) as aqueous solution (perhydrol). This solution is commonly used on various purposes (oxidizing agent, decolourant, disinfectant, antiseptic etc). The present study revealed also the proper conditions for storing H₂O₂ (30%) in order to maintain its maximum efficiency.

Conclusions

The branching factor, (ϕ), and the initiation rate, v_i , increases in the same order:

$$\phi_{UV} > \phi_{Vis} > \phi_{IR}$$

$$v_{iUV} > v_{iVis} > v_{iIR}$$

which supports the photochemical nature of the reaction since the energy associated to the UV radiation is higher (10^2 - 10^4 KJ/mol) than that of the radiations in visible (10^2 KJ/mol) and IR (1 KJ/mol) regions.

- The induction periods decrease in the following order:

$$\lambda_{IR} > \lambda_{vis} > \lambda_{UV}$$

which supports the above conclusion .

- The values of the reaction branching factors, ϕ , between 0.076 - 0.183 min^{-1} are situated within the variation domain found experimentally with the indirect degenerated branching reactions (0.01 - 1 min^{-1}). The obtained result supports this mechanism.

- The study justifies scientifically the conditions of storing H_2O_2 (30%) for maintaining the maximum efficiency when used as oxidizing agent, decolourant or disinfectant.

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