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Chemical Actinometry – a Useful Tool for Light Adsorption in Photochemical Reactors

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Abstract

In the following work we present the elaboration of a mathematical model to determine the adsorption rate of light in a photochemical reactor used for photooxidation of unsaturated fractions C_{10}.

Chemical actinometers with potassium ferrioxalate and uranil acetate were used. A correlation between the wavelength of light radiation and the quantum yield of the photooxidation reaction was obtained.

Keywords: *photooxidation, actinometry, adsorption rate*

Introduction

Chemical actinometers represent a very useful and efficient tool used for determining the quantum yield of a photochemical reaction.
Even so, the chemical actinometers are used to determine light adsorption rate for photochemical reactions. From the chemical actinometers used, potassium ferrioxalate and uranil acetate are the most cited.
In the present work we have studied the adsorption of integral light or monochromatic from an artificial source in a photochemical reactor used to photooxidate unsaturated fractions C_{10}.

Experimental

Experimental installation

For the determination an experimental installation (fig. 1) was used.

The photochemical treatment was carried out in a 150 mL glass reactor, equipped with water refrigeration, magnetic stirrer and oxygenation system. Suspensions formed by 100 mL of C_{10} and 15 mg of photosensitiser were irradiated from the top with a 125 W medium pressure mercury lamp without the glass cover (fluence rate: 15 $Jm^{-2}s^{-1}$ at □ > 254 nm), located at a distance of 12 cm from the solution surface. The system was bubbling with commercial oxygen at flows of about 10 $mL*min^{-1}$, through a sintered glass placed in the bottom of the reactor. For analytical control, samples were taken at convenient times and filtered through a 0.45 □m Milipore filter.

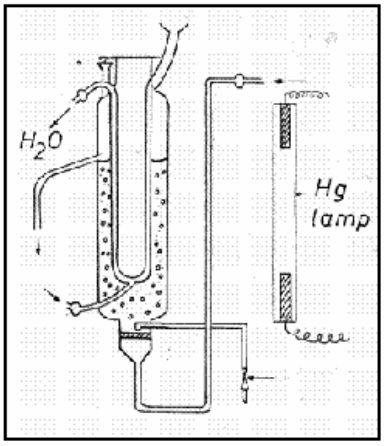

Fig.1. The scheme of the photochemical reactor

Irradiation was realized with a lamp with mercury vapors with 125 W medium pressure, ROMLUX type.

The analysis of the obtained products from the photoreduction reaction of potassium iron oxalate was realized by spectrophotometrical methods [1], and the analysis of the obtained products from the reduction reaction of uranil acetate was realized by a potassium permanganate titration method [2]. The analysis of the reaction products form the photooxidation of the unsaturated fractions C_{10} was realized by iodometrical methods [3].

Materials and apparatus

For the spectral analysis, was used an UV-VIS spectrometer SPECORD M400.

To obtain monochromatic radiations was used a set of interferential filters type KARL ZEISS JENA.

Potassium ferrioxalate used ($K_3Fe(C_2O_4)_3*3H_2O$) was prepared in the laboratory by literature methods [4]. The uranil acetate used was analytical pure Merck reactive.

Unsaturated C_{10} fractions were synthesized in the laboratory by literature methods [5].

As photosensitizer, in order to obtain the photooxidation reaction was used tetraphenilporphirin (TPP) prepared in the laboratory [6].

Benzene has been used as solvent for the TPP solubilisation, purified by drying on metallic sodium and distilled.

Results and Discussion

In a tubular reactor with turbulent flow, the light adsorption rate is determined from the reduction rate of potassium ferrioxalate solution or uranil acetate solution.

The main reactions supported by the two types of chemical actinometers are:

for the potassium ferrioxalate actinometer:

$$K_3Fe(C_2O_4)_3 * 3H_2O \xrightarrow{h\nu} K_3Fe(C_2O_4)_3 + K_2C_2O_4 + CO_2 \quad (1)$$

for the uranil acetate actinometer:

$$\begin{aligned} &UO_2^{2+} + H_2C_2O_4 \rightarrow UO_2^{2+} + CO_2 + HCOOH \\ &UO_2^{2+} + H_2C_2O_4 \rightarrow UO_2^{2+} + CO_2 + CO + H_2O \\ &UO_2^{2+} + H_2C_2O_4 + 2H^+ \rightarrow U^{4+} + 2CO_2 + 2H_2O \end{aligned} \quad (2)$$

For both types of actinometers, the kinetics is:

$$-\frac{dCa}{dt} = \phi\mu\bar{y} \quad (3)$$

Where:

Ca= concentration of Fe^{3+} ions from $K_3Fe(C_2O_4)_3$

= concentration of oxalic acid

t= irradiation time

ϕ =quantum yield

μ= αCa^0 = adsorption factor

$\bar{y}$ = medium intensity of light among the reactor's irradiation surface

η = αCa

α = molar adsorption coefficient

$$\alpha = \sum E(\lambda)T(\lambda) \quad (4)$$

$E(\lambda)$ is the energy from the light source;

$T(\lambda)$ is the reactor's glass transmittance;

By replacing and integration, it can be obtained a calculus relation applicable to both types of chemical actinometers.

$$Cp = \phi\alpha ytCa \qquad \alpha=4000M^{-1}cm^{-1} \quad (5)$$

Cp being the concentration of the reaction products from the methods above (in the case of ferrioxalate actinometer $Cp=C_{Fe2+}$, in the case of uranil acetate actinometer $Cp=C_{CO2}$).

In table 1, are presented the characteristics of mercury vapors lamp of 125 W medium pressure.

Table 1. Lamp characteristics

λ nm	**Radiant energy Einstein/s * 10^8**
365	83
405	40
436	101
546	130
577	103

For the calculus of the intensity of incident monochromatic radiation which goes trough the reactor the following relation is used:

$$y_w = \frac{R^2(-\frac{dc}{dt})}{2\sum\int_0^R \phi_\lambda \cdot \mu_\lambda \cdot \frac{w_\lambda}{w} \cdot F_\lambda(r) \cdot rdr} \quad (6)$$

Where:

R= reactor's radius;

$-\frac{dc}{dt}$ = decomposition speeds of $H_2C_2O_4$ or $K_3Fe(C_2O_4)_3$

$F_\lambda(r)$ = no dimensional profile of radiation

$$F_\lambda(r) = \frac{y_\lambda(r)}{y_w(r)} \quad (7)$$

μ_λ = reaction environment absorbance;

$-\frac{dc}{dt}$ can be determined experimental;

R=3 cm

ϕ = it is known for every λ

η_λ= it is determined experimental at λ;

The results obtained for the studied system are presented in table 2.

Table 2. Light absorption in a photooxidation reaction in the presence of TPP and $K_3Fe(C_2O_4)_3$

λ nm	**$K_3Fe(C_2O_4)_3$**				**$K_3Fe(C_2O_4)_3$+TPP**				
	$-\frac{dc}{dt}$ ***10^6**	**I_0 *10^6**	**I_a *10^6**	**V_{HP}**	$(-\frac{dc}{dt})$ ***10^6**	**I_0 *10^7**	**I_a *10^6**	**V_{HP}**	**I_{TPP}**
	Ms^{-1}	Ms^{-1}	Ms^{-1}	%/h	Ms^{-1}	Ms^{-1}	Ms^{-1}	% h	%
436	1.9	1.74	1.71	0.06	0	6.003	1.8	1.56	36.08
548	2.30	2.3	2	0.1	0.1	7.26	2.2	1.2	17.38
584	1.14	1.14	0.9	0.058	0.137	3.6	1.003	0.7	8.22
polychromatic	8	6.23	6.35	1.2	2.13	2.27	2.23	2	35.11

To determine the medium adsorbed flux, the following relation was followed:

$$I_{abs} = I_0(1-10^{-\varepsilon cl}) \quad (8)$$

The experimental results are presented in table 3.

Table 3. Light absorption in the photooxidation reaction in the presence of TPP

Incident radiation wavelenght	**I_0**	**ε_{TPP}**	**I_{abs}**
nm	**Ms^{-1}*10^6**	**$M^{-1}cm^{-1}$**	**Ms^{-1}*10^6**
436	1.9	$4.78*10^4$	1.9
548	2.30	8100	2.20
584	1.14	3000	1.003
polychromatic	1.6	-	1.35

Table 4. Light absorbtion in the photooxidation reactor

$K_3Fe(C_2O_4)_3$			$UO_2(CH_3COO)_2$	
$(-\frac{dc}{dt})*10^6$	I_0 $*10^6$	λ	$(-\frac{dc}{dt})*10^6$	I_0 $*10^7$
Ms^{-1}	Ms^{-1}	nm	Ms^{-1}	%h
1.9	0.061	436	1.8	6.003
2.30	0.1	548	2.015	7.266
1.14	0.058	584	1.089	3.601
2		polychromatic	2.13	

Table 5. Light absorption parameters in the photooxidation reactor at different radiation

λ	$\phi_\lambda \cdot \mu_\lambda \cdot \frac{w_\lambda}{w} \cdot \int_0^R F_\lambda(r) \cdot rdr$
nm	Mol*m/einstein
436	$2.412*10^{-6}$
548	$1.040*10^{-11}$
584	$0.63*10^{-12}$
integral	$1.6*10^{-7}$

For the same absorption rate of chemical actinometer, I_{abs} by TPP used as sensitizer could be half at a decrease hydroperoxide rate of 0.3% (table 6).

Table 6. Correlation between hydroperoxide concentration, TPP and absorbed light intensity

V_{HP}=1.56%	I_{absTPP}=36.08%	I_a=0.909*Ms^{-1}
V_{HP}=1.2%	I_{absTPP}=17.38%	I_a=0.909*Ms^{-1}

Conclusions

The elaboration of a mathematical model to determine the adsorption rate of light in a photochemical reactor used for photooxidation of unsaturated fractions C10 is presented. Chemical actinometers with potassium ferrioxalate and uranil acetate were used.

All the results proof that by means of chemical actinometers decomposition is possible to evaluate the light absorption in photochemical reactor.

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Actinometria chimică – instrument important în absorbția luminii în reactoare fotochimice

Rezumat

În lucrarea de față se prezintă un model de calcul pentru a determina viteza de absorbție a radiației luminoase într-un reactor fotochimic folosit pentru fotooxidarea fracțiilor nesaturate C_{10}.
Se folosesc actinometrii chimici cu ferooxalat de potasiu şi acetat de uranil. S-a obținut o corelație între lungimea de undă a radiației luminoase şi randamentul cuantic al fotooxidării.