

Equatorial—axial interactions of ligands and photochemical properties of Co(III) complexes containing tetradentate ligands

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The paper presents the results of the photochemical studies of the complexes $trans\text{-}[\text{Co}(\text{L}_{\text{eq}})(\text{L}_{\text{ax}})_2]\text{X}$ in methanol, where $\text{L}_{\text{eq}} = N,N'$ -ethylenebis(acetylacetoniminato) or N,N' -ethylenebis(salicylideniminato) dianion; $\text{L}_{\text{ax}} = \text{NH}_3$ or pyridine; $\text{X}^- = \text{Cl}^-$ or NCS^- . The phenomenon of equatorial—axial interactions of ligands *via* the central atom in complexes forms the basis on which the results are interpreted.

Integral interactions of ligands forming the equatorial plane with those coordinated in axial positions mediated by the central atom (denoted further “eq-ax”) influence the structure, physicochemical properties and reactivity of complexes [1, 2]. Manifestations of eq-ax interactions have been demonstrated for electrochemical properties of Co(II) and Cu(II) complexes [3—5], activation of small molecules [6, 7], and photochemical properties of Fe(III) complexes [8—10].

Based on the study of photochemical properties of some transition-metal complexes containing equatorial tetradentate ligands in dependence on the electronic structure of the central atom, a conclusion stating that an equatorial ligand could influence significantly the ability of an axial ligand—central atom bond to undergo a homolytic or heterolytic splitting, *i.e.* photoredox or photosubstitution reactions of complexes, was drawn. Eq-ax interactions influence both the kinetics [8—10] and thermodynamics [11] of photochemical reactions.

Along with the study of consequences of eq-ax interactions for electrochemical behaviour of cobalt complexes, the consequences of those interactions for photochemical properties of Co(III) complexes have been investigated as well. This paper brings the results obtained within the study of photosubstitution reactions occurring in methanolic solutions of the complexes $trans\text{-}[\text{Co}(\text{L}_{\text{eq}})(\text{L}_{\text{ax}})_2]\text{X}$, where noncyclic tetradentate Schiff base ligands forming the equatorial plane, $\text{L}_{\text{eq}} = N,N'$ -ethylenebis(acetylacetoniminato) or N,N' -ethylenebis(salicylideniminato) dianions are denoted acacen and salen, respectively; ligands bonded in axial positions, $\text{L}_{\text{ax}} = \text{NH}_3$ or pyridine molecules; noncoordinated counter-anions $\text{X}^- = \text{Cl}^-$ or NCS^- .

Experimental

Methanol, anal. grade (Lachema, Brno), was freshly distilled from $\text{Mg}(\text{OCH}_3)_2$ before use. Pyridine, reagent grade (Lachema, Brno), was distilled prior to use. All other chemicals were anal. grade (supplied by Lachema) and used as received.

The compounds H_2acacen and H_2salen were prepared and characterized according to the published procedures [12, 13]. The complexes $\text{trans}[\text{Co}(\text{L}_{\text{eq}})(\text{L}_{\text{ax}})_2]\text{Cl}$ were synthesized and purified as before [14]. ^1H NMR spectra of the complexes correspond to the data given in paper [15]. The complexes $\text{trans}[\text{Co}(\text{L}_{\text{eq}})(\text{L}_{\text{ax}})_2]\text{NCS}$ were prepared by metathetic reaction of the corresponding chlorides with an excess of KNCS in methanol. After insoluble KCl was filtered off, methanol was removed *in vacuo* and the crude solid complexes were recrystallized from methanol. Analyses of the complexes and Schiff bases H_2acacen and H_2salen for the content of carbon, nitrogen, and hydrogen were in good agreement with the calculated values. The content of cobalt was determined in the complexes spectrophotometrically in the form of $[\text{Co}(\text{NCS})_4]^{2-}$ after the quantitative reduction of Co(III) to Co(II) with solid L-ascorbic acid. To such Co(II)-containing solution (usually 5 cm^3), 10 cm^3 of 50% aqueous solution of NH_4NCS was added and the solution was filled up to 25 cm^3 volume with acetone cooled to 5°C . From the values of absorbance at $\lambda = 625\text{ nm}$ ($\epsilon_{625\text{ nm}} = 175\text{ m}^2\text{ mol}^{-1}$ [16]) the content of cobalt in each complex was calculated (Table 1). In a similar manner the content of Co(II) was determined in irradiated solutions.

Table 1

Calculated and determined content of cobalt in the prepared complexes and the initial rates of the photoreduction of Co(III) to Co(II)

Complex	$w_{\text{Co}}(\text{calc.})/\%$	$w_{\text{Co}}(\text{found})/\%$	$\frac{dn_{\text{Co(II)}}}{dt} / (10^{-7}\text{ mol min}^{-1})$
$\text{trans}[\text{Co}(\text{acacen})(\text{NH}_3)_2]\text{Cl H}_2\text{O}$	15.98	15.71	2.3 ± 0.3
$\text{trans}[\text{Co}(\text{acacen})(\text{NH}_3)_2]\text{NCS}$	15.79	15.63	2.3 ± 0.3
$\text{trans}[\text{Co}(\text{acacen})(\text{py})_2]\text{Cl}$	12.41	12.77	4.7 ± 0.2
$\text{trans}[\text{Co}(\text{acacen})(\text{py})_2]\text{NCS}$	11.85	11.88	4.4 ± 0.2
$\text{trans}[\text{Co}(\text{salen})(\text{NH}_3)_2]\text{Cl}$	14.92	15.20	2.9 ± 0.3
$\text{trans}[\text{Co}(\text{salen})(\text{NH}_3)_2]\text{NCS}$	14.12	14.15	2.3 ± 0.4
$\text{trans}[\text{Co}(\text{salen})(\text{py})_2]\text{Cl H}_2\text{O}$	10.97	10.91	2.3 ± 0.1
$\text{trans}[\text{Co}(\text{salen})(\text{py})_2]\text{NCS}$	10.88	10.83	3.2 ± 0.8

Formaldehyde was identified as 3,5-diacetyl-1,4-dihydrolutidine (formed by reaction of formaldehyde with a specific reagent containing 150 g of $\text{NH}_4\text{CH}_3\text{COO}$, 3 cm^3 of CH_3COOH , and 2 cm^3 of acetylacetone in 1 dm^3 of aqueous solution) for which at an absorption maximum $\epsilon_{412} = 800\text{ m}^2\text{ mol}^{-1}$ [17].

Methanolic solutions of Co(III) complexes were irradiated with light at $\lambda = 313\text{ nm}$ in a three-compartment quartz photoreactor (light emitted by a medium-pressure

mercury 125 W lamp Tesla RVK was monochromatized using a solution filter prepared according to [18]) or with unfiltered light of the said lamp. The intensity of nearly monochromatic incident light, passed through the solution filter into a studied system, was $I_0(313 \text{ nm}) = 4.4 \times 10^{-4} N_A h\nu \text{ min}^{-1}$ as determined by a potassium trisoxalatoferrate(III) actinometer [19]. Solutions were irradiated in argon atmosphere and kept at $(25 \pm 2)^\circ\text{C}$.

The course of photochemical reactions was monitored spectrophotometrically as follows: 2 cm^3 of a sample solution was withdrawn from the irradiated system (initial volume of 140 cm^3) after certain intervals of irradiation; electronic absorption spectra were recorded, Co(II) was determined, and formaldehyde identified in the sample. Electronic absorption spectra of the studied systems being in dark did not undergo changes.

Electronic absorption spectra were scanned on Specord M-40 and Specord UV VIS spectrophotometers (Zeiss, Jena). ^1H NMR spectra of saturated solutions of the complexes in CD_3OD were recorded on a Varian VXR 300 spectrometer using $(\text{CH}_3)_4\text{Si}$ as an internal reference.

Experimental data (dependences of absorbance on time of irradiation; calculation of quantum yield values) were evaluated by the least-square method.

Results

Photochemical properties of the system of the complex $\text{trans}[\text{Co}(\text{acacen})(\text{NH}_3)_2]\text{Cl} \cdot \text{H}_2\text{O}$

Irradiation of methanolic solutions of $\text{trans}[\text{Co}(\text{acacen})(\text{NH}_3)_2]\text{Cl} \cdot \text{H}_2\text{O}$ ($c = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$) at $\lambda = 313 \text{ nm}$ gives rise to the spectral changes as

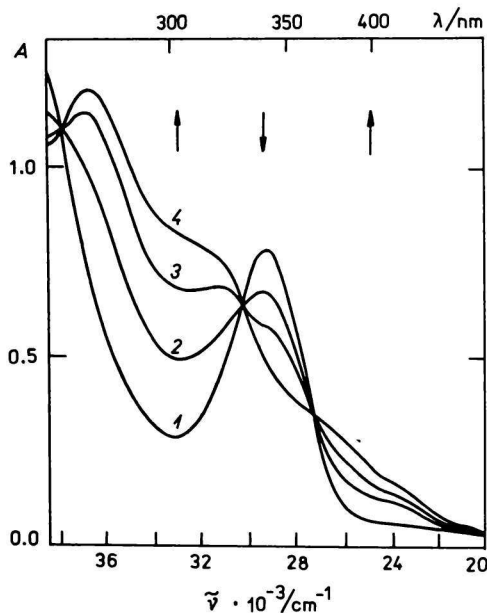


Fig. 1. Electronic absorption spectral changes accompanying the photolysis of $\text{trans}[\text{Co}(\text{acacen})(\text{NH}_3)_2]\text{Cl} \cdot \text{H}_2\text{O}$ in methanol. $I_0(313 \text{ nm}) = 4.4 \times 10^{-4} N_A h\nu \text{ min}^{-1}$. The arrows represent the increase (decrease) of absorbance during irradiation. Time intervals of irradiation: 1. 0 min, 2. 20 min, 3. 47 min, 4. 120 min or 220 min.

shown in Fig. 1. Three isosbestic points (at 263, 330, and 363 nm) are present in the region of $\lambda = 260\text{--}800$ nm. Before irradiation the absorbance of the solution at 313 nm was $A_{313} = 0.36$. Changes in the spectra occur during 120 min of irradiation, further irradiation (100 min) does not induce spectral changes. The same spectral changes as observed using the incident light with the wavelength 313 nm, were observed when irradiating the system with polychromatic light (320—600 nm). In the latter case, however, the rate of the changes was higher.

The course of photochemical reaction was monitored at $\lambda = 306$ nm (a region of a substantial spectral change as shown in Fig. 1). At this wavelength the values of the molar absorption coefficients are $\epsilon_{306}(\text{R}) = 290 \text{ m}^2 \text{ mol}^{-1}$ for the reactant (parent complex *trans*-[Co(acacen)(NH₃)₂]Cl · H₂O) and $\epsilon_{306}(\text{P}) = 830 \text{ m}^2 \text{ mol}^{-1}$ for the product of the photochemical reaction. The quantum yield value of the photochemical reaction Φ was calculated from the plot of the absorbance A_{306} of the irradiated system at monitoring wavelength of 306 nm *vs.* time of irradiation t_{irr} (Table 2) according to the relation (see Appendix)

$$\Phi = \frac{V}{l[\epsilon_{306}(\text{P}) - \epsilon_{306}(\text{R})]I_0(313 \text{ nm})(1 - 10^{-A_{313}})} \frac{dA_{306}}{dt}$$

where V is the initial volume of the irradiated solution ($V = 0.14 \text{ dm}^3$); l is the path length of cell ($l = 1 \text{ cm}$); dA_{306}/dt is the rate of the absorbance change at $t_{\text{irr}} = 0$ ($dA_{306}/dt = (1.09 \pm 0.20) \times 10^{-2} \text{ min}^{-1}$); the values of the other quantities are given above. Using the relationship, the quantum yield value was calculated as $\Phi = (1.1 \pm 0.2) \times 10^{-3}$

Table 2

Dependence of the absorbance of irradiated *trans*-[Co(acacen)(NH₃)₂]Cl · H₂O in methanol on the time of irradiation

$t_{\text{irr}}/\text{min}$	0	10	20	30	47	65	85	120	180	220
A_{306}	0.29	0.40	0.50	0.59	0.69	0.75	0.79	0.83	0.83	0.83

During the irradiation of the system at $\lambda = 313$ nm, neither Co(II) nor CH₂O is formed. ¹H NMR spectra of the parent complex *trans*-[Co(acacen)(NH₃)₂]Cl · H₂O and of the product of photochemical change, measured in CD₃OD are nearly equal and consist of peaks at 5.08, 4.92, 3.80, 3.37, 3.13, 2.28, 2.14, and 1.32 (chemical shifts δ *vs.* (CH₃)₄Si).

Irradiation of methanolic solutions of the complex with unfiltered radiation of a medium-pressure mercury lamp or a low-pressure mercury lamp (which emits predominantly the light with the wavelength 253.7 nm) leads to the photoreduction of Co(III) to Co(II). Table 3 offers the results obtained for the

system in which $c(\text{Co(III)}) = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$, irradiated by unfiltered light of a medium-pressure mercury lamp. Evaluation of the data yields the initial rate of Co(III) photoreduction being $(2.3 \pm 0.3) \times 10^{-7} \text{ mol min}^{-1}$. In the system formaldehyde was identified.

Table 3

Dependence of the absorbance of systems^a on the time of irradiation

$t_{\text{irr}}/\text{min}$	0	8	15	24	33	47	70
A_{625}	0.025	0.080	0.125	0.160	0.190	0.210	0.240

^a 4 cm³ of irradiated methanolic solution of *trans*-[Co(acacen)(NH₃)₂]Cl · H₂O + 8 cm³ of 50% aqueous solution of NH₄NCS + acetone up to 25 cm³

Table 4

Experimental data on the systems irradiated in time periods t_{irr} after which a further irradiation does not lead to spectral changes

Complex	λ_{vis}	λ_{R} (ϵ)	λ_{p} (ϵ)	$t_{\text{irr}}/\text{min}$	$\Phi \cdot 10^3$
[Co(acacen)(NH ₃) ₂]Cl · H ₂ O	263	340 (790)	270 (1210)	120	1.1 ± 0.2
	330		320 sh		
	363		395 sh 425 sh		
[Co(acacen)(NH ₃) ₂]NCS	263	340 (790)	270 (1200)	120	1.3 ± 0.2
	330		320 sh		
	364		395 sh 425 sh		
[Co(acacen)(py) ₂]Cl	275	340 (600)	318 (1210)	30	2.7 ± 0.2
	335		370 sh		
	365		430 sh		
	435				
[Co(acacen)(py) ₂]NCS	275	340 (600)	320 (1190)	30	2.5 ± 0.2
	336		370 sh		
	365		430 sh		
	440				
[Co(salen)(NH ₃) ₂]Cl	300	285 sh	333 (780)	25	4.5 ± 0.3
			320 sh 388 (550)		
			395 sh		
[Co(salen)(NH ₃) ₂]NCS	300	285 sh	333 (785)	25	4.4 ± 0.2
			320 sh 390 (550)		
			395 sh		
[Co(salen)(py) ₂]Cl · H ₂ O	318	385 (575)	335 (605)	30	3.4 ± 0.4
	370		380 sh		
	425		430 sh		
[Co(salen)(py) ₂]NCS	320	387 (570)	335 (610)	30	3.5 ± 0.2
	370		380 sh		
	425		430 sh		

Photochemical properties of the systems of the trans-complexes
 [Co(acacen)(NH₃)₂]NCS, [Co(acacen)(py)₂]Cl, [Co(acacen)(py)₂]NCS,
 [Co(salen)(NH₃)₂]Cl, [Co(salen)(NH₃)₂]NCS, [Co(salen)(py)₂]Cl,
 [Co(salen)(py)₂]NCS

Photochemical properties of the above complexes were followed in a similar manner to that of the *trans*-[Co(acacen)(NH₃)₂]Cl · H₂O.

Irradiation of methanolic solutions of the complexes at $\lambda = 313$ nm gave rise to the spectral changes analogous to those of the former complex. Positions (in nm) of isobestic points λ_{is} , band maxima, and shoulders in electronic absorption spectra of the parent complexes λ_R , and of the products λ_P of photochemical changes and the corresponding values of the molar absorption coefficients $\varepsilon/(\text{m}^2 \text{mol}^{-1})$ together with the calculated quantum yield values Φ of the photochemical changes are listed in Table 4.

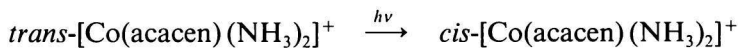
Unfiltered light emitted by a medium-pressure mercury lamp induces in methanolic solutions of the complexes ($c(\text{Co(III)}) = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$) the photoreduction of Co(III) to Co(II) and the formation of CH₂O. The initial rates of Co(II) formation calculated from the dependences of the amount of substance of Co(II) on irradiation time are summarized in Table 1.

Discussion

Co(III) complexes undergo, in general, three types of photochemical reactions [18, 20]: photosubstitutions, photoisomerizations, and photoredox processes. Which of these modes of photochemical changes occur, it depends on the composition and structure of a complex, type of photoreactive excited state, and conditions of the realization of the photochemical change. The changes occurring in our irradiated systems may be, in principle, a consequence of any type of photoreaction.

Since no formation of Co(II) and CH₂O was observed when the systems were irradiated at $\lambda = 313$ nm, the observed spectral changes could not be attributable to photoredox reaction, *i.e.* the photoreduction of Co(III) to Co(II) was not realized.

It follows from the presence of isobestic points in the spectra of all irradiated systems that during irradiation there are only two Co(III) complexes in the systems: a parent complex (reactant) and a product of photoreaction. The product may differ from the reactant either in its structure, *i.e.* the spectral changes are due to an isomerization reaction, for example

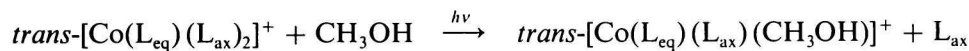


or in the composition, which means that the product was formed by a photosubstitution.

The tetradentate ligands acacen and salen can be coordinated to the central atom Co(III) forming the equatorial plane (complexes of *trans* configuration) or the nitrogen donor atoms can be bonded in *cis* position in the plane perpendicular to that formed by the central atom and oxygen donor atoms. The latter mode of coordination was found in complexes containing a bidentate ligand in the coordination sphere (such as 1,10-phenanthroline, 2,2'-bipyridine, 1,2-diaminoethane) [15]. ^1H NMR spectra of the parent complex *trans*-[Co(acacen)(NH₃)₂]⁺ and of the product of its photochemical change coincide and consist of peaks corresponding to in-plane bonded acacen ligand [15] (the peak at $\delta = 5.08$ is attributed to C=CH; at 3.13 to CH₂—CH₂; at 2.28 to CH₃CO, and at 2.14 to CH₃—CN in the complex with *trans* coordination). The changes in electronic absorption spectra of the system of the complex *trans*-[Co(acacen)(NH₃)₂]Cl · H₂O induced by light with the wavelength 313 nm are not, therefore, a consequence of *trans* → *cis* isomerization. The same conclusion was accepted for systems of the other complexes, as well. The conclusion emerges also from the fact of the existence of *cis* complexes only in cases when they contain a bidentate ligand. A further evidence against *trans* → *cis* photoisomerization comes from the observation [21] that irradiation of pyridine solutions of the complexes *trans*-[Co(L_{eq})(py)₂]⁺ does not lead to any spectral changes.

As a consequence of a heterolytic central atom—ligand bond splitting, the releasing of equatorial ligand (the process is, however, excluded by ^1H NMR spectra), one or both axial ligands may occur. A stepwise substitution of both *N*-donor axial ligands would not lead to the presence of isosbestic points in the spectra. Moreover, a simultaneous exchange of two ligands in the coordination sphere of complexes is not known [18, 20]. Such substitution (which is possible from the viewpoint of theory) should produce the identical product from the parent complexes containing the same equatorial ligand and different axial ligands, which, however, was not observed in the spectra of corresponding pairs of complexes ([Co(acacen)(NH₃)₂]⁺ and [Co(acacen)(py)₂]⁺, or [Co(salen)(NH₃)₂]⁺ and [Co(salen)(py)₂]⁺) as it follows from Table 4.

Based on the interpretation of the experimental results it can be stated that irradiation of the systems of the studied complexes at $\lambda = 313$ nm leads to the substitution of one *N*-donor axial ligand by a solvent molecule



The given reaction is in accord with the observed fact [21] that no changes in electronic absorption spectra are realized when irradiating pyridine solutions of

the complexes and, therefore, pentacoordinate complexes are not formed as final product of photosubstitutions. It follows from the spectra (Table 4) that the counter-anions Cl^- or NCS^- do not enter the coordination sphere and they do not influence the course of the photosubstitution reactions.

By the absorption of a photon at $\lambda = 313 \text{ nm}$, the spin-allowed singlet intraligand ($\text{IL}_{\pi-\pi^*}(\text{C}=\text{N})$) or L_{ax} MCT excited states of Co(III) complexes are populated [22]. The long-lived spin-forbidden triplet L_{ax} MCT or LF states can be reached by subsequent internal conversion of the intersystem crossing processes. In both cases of formed excited states the electron density increases along the axial coordinate (z axis) as unoccupied orbitals in Co(III) complexes are the $\text{Co}3d$ orbitals localized along the z axis [23]. Compared with the ground state of the complexes, the interelectronic repulsion is stronger in the involved excited states, which improves conditions for the splitting of a bond of the central atom and an axial ligand.

Irradiation of the systems of the complexes with polychromatic radiation emitted by a medium-pressure mercury lamp leads to the photoreduction of Co(III) to Co(II) which fits knowledge on photochemical properties of Co(III) complexes [18, 20]. Medium-pressure mercury lamps produce short-wavelength light [19] (222.4, 253.7, 296.7, 265.3, and 302.6 nm in addition to low-energy photons) able to reduce Co(III) to Co(II). Mechanism of photoredox processes is usually not simple. In our investigated systems, formaldehyde (as the final product of methanol oxidation) and Co(II) were present. Analogous formation of Co(II) was found in the systems of the complexes irradiated by a low-pressure mercury lamp, which emitted radiation mainly of 253.7 nm. Instead of such a lamp (its intensity is rather low being $I_0(253.7 \text{ nm}) = 1.0 \times 10^{-5} N_A h\nu \text{ min}^{-1}$) polychromatic light of a medium-pressure lamp was used to monitor the photoredox deactivations (Table 1) due to the low quantum yield of the Co(III) photoreduction. The presented results document that photochemical reactivity of a ligand coordinated in the axial position of the Co(III) complexes is influenced by the ligand forming the equatorial plane. This observation is in agreement with envisages concerning consequences of eq-ax interactions of ligands *via* the central atom for the properties of complexes [1, 2]. Along with the results obtained in the framework of the study of photoredox reactions of Fe(III) complexes [8–10], the results presented in this paper show that the phenomenon of eq-ax interactions is reflected both for complexes in their ground state and excited states.

Appendix

The relation for the calculation of quantum yield values was derived on the basis of presumption of the presence of two light-absorbing species in inves-

tigated systems: the parent complex R and the product of its photochemical change P. The total solute concentration given by

$$c = c(\text{R}) + c(\text{P})$$

is time-independent. The absorbance of a system $A_{\lambda m}$ at monitoring wavelength λm can be expressed as

$$A_{\lambda m} = l[\varepsilon_{\lambda m}(\text{R})c(\text{R}) + \varepsilon_{\lambda m}(\text{P})(c - c(\text{R}))]$$

and its change in time obeys the equation

$$\frac{dA_{\lambda m}}{dt} = \frac{dc(\text{R})}{dt} [\varepsilon_{\lambda m}(\text{R}) - \varepsilon_{\lambda m}(\text{P})] l$$

where l is the optical path of cell (in cm); $\varepsilon_{\lambda m}(\text{R})$ and $\varepsilon_{\lambda m}(\text{P})$ are the molar absorption coefficients of the reactant R and the product P at the monitoring wavelength.

The quantum yield of product formation Φ is defined as

$$\Phi = \frac{\frac{dn(\text{P})}{dt}}{I_{\text{abs}}}$$

where $dn(\text{P})/dt$ is the amount of product formed per unit time (in mol min⁻¹) and I_{abs} is amount of photons absorbed by reactant per unit time (in $N_A h\nu$ min⁻¹). Quantities $dc(\text{R})/dt$ and $dn(\text{P})/dt$ are related by

$$\frac{dn(\text{P})}{dt} = -V \frac{dc(\text{R})}{dt}$$

where V denotes the volume of irradiated solution (in dm³). Expressing the intensity of light absorbed by irradiated solution at the wavelength of incident light λi

$$I_{\text{abs}}(\lambda i) = I_0(\lambda i)(1 - 10^{-A_{\lambda i}})$$

(in which $I_0(\lambda i)$ is the intensity of incident light determined by actinometry; $A_{\lambda i}$ is the absorbance of the system at the wavelength of incident light) the relation for quantum yield values calculation can be rearranged into the expression

$$\Phi = \frac{V}{l[\varepsilon_{\lambda m}(\text{P}) - \varepsilon_{\lambda m}(\text{R})] I_0(\lambda i)(1 - 10^{-A_{\lambda i}})} \frac{dA_{\lambda m}}{dt}$$

It follows from the definition of quantum yield that it should be expressed in mol of product/mol of photons. Conventionally it is, however, expressed as a dimensionless quantity.

For the irradiated system containing the *trans*-[Co(acacen)(NH₃)₂]Cl H₂O, $\lambda_m = 306$ nm. It should be noted that whatever wavelength can be taken as a monitoring one except of the wavelength of isosbestic points.

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