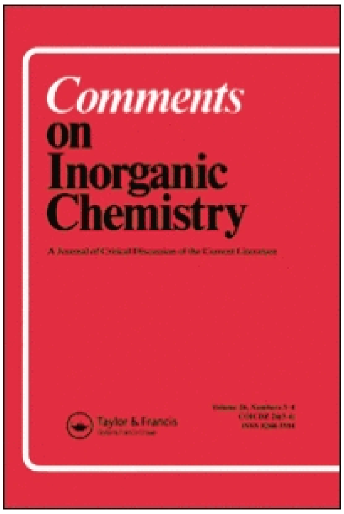

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Correlations Between Excited-State Reactivity Parameters and Ground-State Characteristics of Complexes-Are They Justifiable?

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Correlations Between Excited-State Reactivity Parameters and Ground-State Characteristics of Complexes—Are They Justifiable?

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This article appraises the possibility and justification for searching out correlations between excited-state photoredox reactivity parameters (quenching constant k_q, threshold energy E_{th}, quantum yield ϕ) and ground-state parameters (such as ionization energy I, optical electronegativity x, redox potential E^0, Taft parameters σ_T and Hammett parameters σ_H) of complexes, their ligands and central atoms. Based on experimental data this paper deals with the question of whether the existence of such correlations, and in which cases, can be justified.

Key Words: *photochemistry, reactivity, electron transfer, photoredox reactions*

INTRODUCTION

One of the main tasks and goals of chemistry is the acquisition of the ability to predict and purposefully modify the structure and reactivity of chemical compounds and materials. To approach such a state of the art, relationships between various factors controlling properties of chemical compounds are being gradually unveiled, a

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number of empirically found and theoretically rationalized relations between the structure, physico-chemical properties and chemical behaviour is steadily increased and the level of their understanding and interpretation improved.[1,2]

In the field of coordination chemistry researchers manipulate a set of parameters, approaches and rules enabling them to predict and rationalize a lot of structure–property dependences, spectral and magnetic properties, course of chemical transformations, and so on.

Mastering the general laws of chemistry, rules of chemical behaviour, and absorbing chemistry as a system of mutually conditioned phenomena create in chemists particular qualities called chemical thinking, intuition and sense. These qualities have been based on knowledge of the ground-state properties of chemical substances and have been successfully exploited in ground-state chemistry. This orientation and limitation of chemical thinking is quite understable as the overwhelming majority of experiments and theoretical descriptions on molecular and crystal structures, electron density distribution, thermodynamic properties and physico-chemical parameters concern molecular species and compounds in their ground electronic state. Notwithstanding that the ground state is the most common state for chemistry, it is only one of the set of existing states, the other being electronically excited states.

Molecules and ions in electronically excited states (further on abbreviated as "ES") can differ substantially from those in the ground state (further on "GS"). A GS → ES transition is associated with changes in structure, acid–base and redox properties, energy content, dipole moment, electron and/or spin configuration, lifetime and other properties.[3] All these changes are reflected in different chemical behaviour of molecules in ES compared to those in the GS. This is the main reason why molecules in ES are regarded as new chemical species.

In photochemistry of coordination compounds (and in photochemistry in general) three experimental parameters quantifying and related to photochemical reactivity are used:

1. rate constant k_q—a kinetic parameter of monomolecular or bimolecular quenching of an excited state,

2. quantum yield ϕ—a statistical-kinetic parameter of the efficiency of a deactivation process,
3. threshold energy E_{th}—a quasi-thermodynamic parameter, the photon energy at which the quantum yield of the given deactivation process approaches zero value.

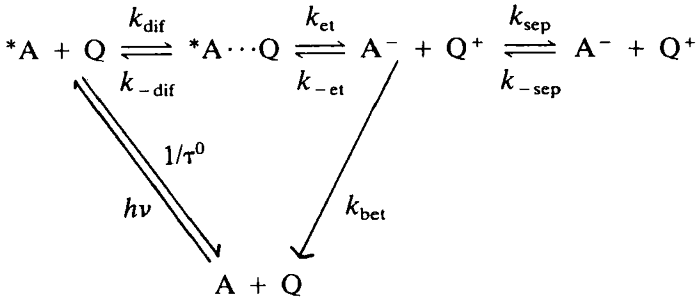
There are some more or less successful attempts to empirically find and theoretically explain correlations between the above ES reactivity parameters and GS properties of complexes, their central atoms and ligands. One of the aims of such attempts is to exploit structure-photoreactivity relationships for practical purposes. Frequently, however, common chemical intuition and sense fail in the prediction of photoreactivity.[4]

In this paper the attention will be focused on photoredox reactions of coordination compounds, particularly on outer-sphere electron-transfer processes and intramolecular decomposition; as for other types of photoredox reactions (redox isomerizations, formation and decomposition of polynuclear complexes, ligand-localized changes) suitable data can very seldom be found in the literature.[3,5-7]

RATE CONSTANT k_q

The rate constant k_q is an experimental quantity obtainable by fast (flash) techniques, usually in nano- and picosecond time scales. So far, the ES–GS dependences, treated in detail, are evaluated almost exclusively for outer-sphere electron-transfer processes occurring often in the systems, irradiation of which does not lead to any net chemical change due to a fast back electron transfer. The corresponding bimolecular quenching constant k_q used to be related to the electron-transfer process involving one of the reactants (complex) in its excited state (denoted *A) and its reaction partner Q in the ground state.[8] The rate constant k_q has been correlated with the redox potentials E^0 or ionization energies I, both being GS parameters of the reactants.

The elementary steps involved in a reversible outer-sphere electron-transfer reductive quenching (oxidative outer-sphere quenchings, energy transfer processes and intramolecular electron-transfer deactivations[9] can be treated in a similar manner) are represented in the following Scheme:



Based on some theoretically reasonable assumptions (for details see Refs. 8 and 10) various functions $k_q = f(\Delta G^0_{et})$ have been derived. Of all the approaches (classical Marcus, semiempirical Rehm–Weller, the latest quantum-mechanical) the best fitting of experimental and calculated dependences of the ES parameter log k_q versus GS parameter ΔG^0 (depending predominantly on the values of the redox potentials $E^0(^*A/A^-)$ and $E^0(Q^+/Q)$) is provided by the Rehm–Weller approach which is also the most frequently used. The potential $E^0(^*A/A^-)$ can be expressed through the SI units as follows:

$$E^0(^*A/A^-) = E^0(A/A^-) + Nh\nu/F$$

where N is the Avogadro's constant, F is the Faraday constant, $h\nu$ is the energy of the O–O transition, i.e., the difference in electronic energy content of *A and A molecules.

For a closely related family of redox partners Q, having variable redox potential values $E^0(Q^+/Q)$, similar size and charge, it is possible to predict the shape of the log k_q–$E^0(Q^+/Q)$ curve, or at least, to compare the k_q value for a given quencher with its neighbours in the E^0-value sequence. A typical calculated plot of log k_q vs. $E^0(Q^+/Q)$ together with the experimental data is exhibited in Fig. 1 (curve a) for the reductive quenching of $^*[Cr(bpy)_3]^{3+}$ by aromatic amines and methoxybenzenes.[11] The curve (and it is a general feature of such dependences) consists of three parts[8]: an

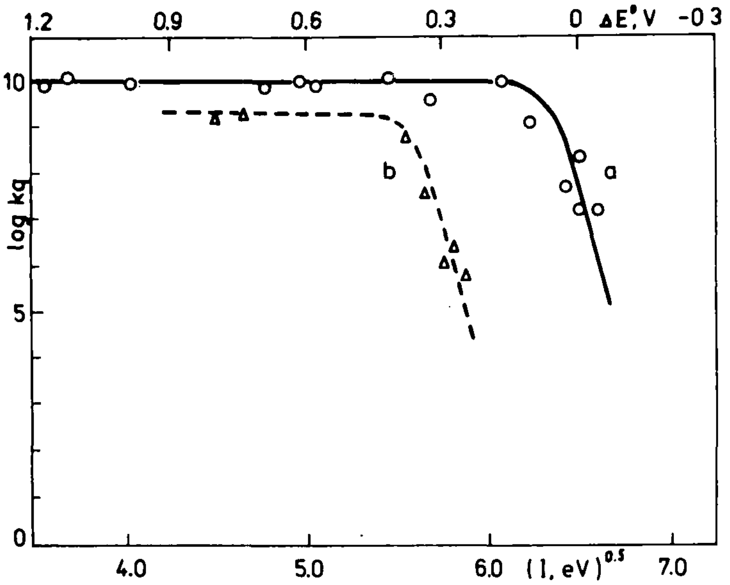


FIGURE 1 Plots of log k_q vs. ΔE^0 (top scale) for the reductive quenching of $^*[\mathrm{Cr(bpy)_3}]^{3+}$ by aromatic amines and methoxybenzenes (Ref. 11) (circles denote experimental values, curve a represents the plot calculated according to Rehm–Weller; $E^0 = E^0(\mathrm{Q^+/Q}) - E^0(^*[\mathrm{Cr(bpy)_3}]^{3+/2+})$) and of log k_q vs. the square root of the ionization energy (bottom scale) of various metal cations (Ref. 12) (triangles Δ, curve b).

Arrhenius-type portion in the endoergonic region; an intermediate region in which log k_q increases in a complex but monotonous way as ΔG decreases (the region centered at $\Delta G = 0$); and a plateau in the exoergonic region in which the value of log k_q approaches the value of k_{dif}.

In spite of the fact that some questions are still open to discussion (e.g., the Marcus inverted region) a conclusion can be drawn stated that ES–GS relations involving bimolecular quenching rate constant k_q as an ES parameter and redox potentials of the reactants as GS parameters are for outer-sphere electron transfer reactions both rationalizable and justifiable. Although a deep knowledge of the above processes and correlations is of minor importance for applied photochemistry at present it seems to be a crucial point for understanding the intimate mechanisms and pathways of chemical transformations.

A similarly featured curve, as generally found for k_q–ΔE^0 dependences, was observed[12] when plotting the log k_q of the excited uranyl $^*UO_2^{2+}$ reductive quenching versus the square root of the gas-phase ionization energy $I(M^{n+})$ of several metal cations M^{n+} acting as quenchers (Fig. 1, curve b). A theoretical base for such correlations stems from the assumption[13] that an electron transfer step occurring by the tunneling mechanism is a fast one during which any substantial change in the hydration shell of the cations does not occur and, according to the authors,[13] solution $E^0(M^{n+1}/M^{n+})$ values may be substituted by gas-phase $I(M^{n+})$ values.

There are, however, at least two points casting doubt upon such an approach. The first one arises out of a very simple but illustrative calculation based on the values $E^0(^*UO_2^{2+}/UO_2^{+}) = 2.6$ V (which corresponds to $\Delta G^0 = -251$ kJ mol^{-1} at the reduction) and the values of ionization energies being $I(M^{n+}) > 2{,}000$ kJ mol^{-1}. It is obvious that taking only the above values into account, the related electron-transfer quenching would be too endoergonic to proceed. The second problem concerns the authors' assumption itself. The hydration energy varies strongly with the charge and polarizability of the cations M^{n+} and therefore cannot be taken as a constant free energy contribution to the stability of the cations.

It can be concluded that even if a Rehm–Weller type dependence was observed in a certain system it does not seem to be appropriate and justifiable to substitute solution E^0-values for free-particle I-values and to correlate the latter GS parameters with the ES parameter k_q for redox processes occurring in the solutions.

THRESHOLD ENERGY E_{th}

Threshold energy E_{th} has been determined and correlated with GS parameters of complexes in a few cases only. As a quantity related to the individual bond splitting energies[14] threshold energy is of importance for both the theory and practical aspects of photochemistry (it informs, e.g., which wavelengths of radiation cannot be used to prevent undesirable reactions from occurring). In spite of the possibilities offered by wavelength-tunable lasers and its importance, threshold energy still remains on the periphery of photochemists' interest.

In his pioneering works Endicott determined the E_{th} value for inner-sphere photoredox reactions of the complexes $[Co(NH_3)_5X]^{2+}$ and some other cobalt(III) complexes.[14-17]

Plotting E_{th} values versus various GS parameters of the acidoligands X^- (redox potentials E^0 for the reduction of the complexes are not, due to a strong irreversibility of the process, known) the correlation of the E_{th} values with the optical electronegativity $x(X^-)$ seems to be the best one (see data in Table I).

For the complexes trans-$[Fe(MC)X_2]^+$, where MC denotes pentaazamacrocyclic ligands, the linear dependence of the threshold energy for X^- oxidation associated with Fe(III) photoreduction, on the ionization energy of the acidoligands X^- was observed[18] (it is interesting that the redox potential value E^0 of electrochemical reduction of the complexes is almost independent of the ligands X^-).

It should be mentioned that the number of complexes in each of the investigated families is small and does not allow us to formulate a more general conclusion. It may be tentatively said that correlations of E_{th} as ES parameter with some GS parameters could exist and we believe they will be explained and justified by theory.

The data collected in Table I manifest that the E_{th} values can be correlated with ligand (complex) GS parameters only within a very closed family of compounds (see, e.g., the difference in the E_{th} values for a homolytic splitting of an Fe(III)–X^- bond in the complexes having the same chromophore, the same axial, but different equatorial, ligands [15]pydieneN$_5$ a [15]pyaneN$_5$). Of course even in a series of similar complexes, such as $[Co(NH_3)_5X]^{2+}$, the influence of one ligand (in the discussed case it is the redox changed X^-) on the other ligands cannot be omitted. In other words, the properties of the fragment $[Co(NH_3)_5]^{3+}$ will vary depending on the properties of the ligands X^-. To take them as a constant factor is a useful but more or less rough approximation.

Obviously, the work started by Endicott needs successors in order to build up a good theoretical background for understanding and correlating the ES parameter threshold energy with GS parameters of complexes.

TABLE I

Ground-state properties (I—ionization energy; x—optical electronegativity; E^0—redox potential) and excited-state parameters of photoredox decompositions (E_{th}—threshold energy; ϕ^{OS} and ϕ^{IS}—quantum yields of outer-sphere and inner-sphere reactions, respectively) of acidoligands X^- and their Fe(III) and Co(III) complexes (tabulated energy values in eV; E^0 for X^- in V vs. aqueous NHE, for the Co(III) complexes in V vs. NHE in CH_3CN).

	Ground-State Properties							
Ligand X^-	Cl^-	Br^-	NCS^-	SCN^-	I^-	N_3^-	NO_2^-	Ref.
$x(X^-)$	2.83	2.74	2.61	2.53	2.21	2.77	2.60	15
$I(X^-)$	3.61	3.36	2.13	2.13	3.06	2.70	2.38	20
$E^0(X/X^-)$	2.41	1.92	1.63	1.63	1.33	1.33	1.04	21
$E^0([Co(dieneN_4)X_2]^{+/0})$	−0,20	0.17	0.44	–	–	−0.45	−0.40	17
			Threshold Energies E_{th}					
$[Co(NH_3)_5X]^{2+}$	3.21	2.69	2.95	2.45	2.05	2.68	2.57	15
$[Fe([15]pydieneN_5)X_2]^+$	3.82	3.21	2.34	–	–	2.86	–	18
$[Fe([15]pyaneN_5)X_2]^+$	4.85	4.27	–	–	–	3.77	–	18
			Quantum Yields for $[Co(NH_3)_5X]^{2+}$					
ϕ^{IS}, 254 nm	0.25	0.33	0.13	–	0.99	0.20	0.51	5
ϕ^{IS}, 365 nm	traces	0.15	0.026	–	0.47	0.44	0.31	5
ϕ^{OS}, 365 nm	0.4	0.5	–	–	–	0.28	0.64	22
ϕ^{OS}, 436 nm	0.5	0.23	–	–	–	0.3	0.55	22
ϕ^{OS}, 475 nm	0.3	0.6	–	–	–	–	0.29	22
			Quantum Yields for $[Co(dieneN_4)X_2]^+$					
$\phi_{Co(II)}$, 315 nm	0.35	0.11	0.06	–	–	0.20	–	23

QUANTUM YIELD ϕ

Quantum yield is the most frequently used and easily accessible ES reactivity parameter. It is also the most important from a practical point of view because it represents the measure of the efficiency of a given deactivation mode, and when using light as a reactant it can be taken as an economic parameter. Some examples may be helpful to document the matter.

The primary quantum yield of a radical photoformation on the one hand, and consumption on the other hand, determines the possibility of utilizing photosensitive compounds as either initiators of radical polymerization processes or photostabilizers. The ability of a compound to act as a photocatalyst is conditioned by a high efficiency of the required photoreactions.

A high overall quantum yield of endoergonic net photoreactions is a necessity for effective conversion and storage of solar energy (fast recombination reactions are one of the main obstacles to reach success in this field). The use of photochemistry as a tool for preparation of new compounds depends, besides their selectivity, on a high quantum yield of the corresponding photoreactions.

Those mentioned and other practical tasks are, along with theoretical ones, the main reasons for searching out factors and modes of how to predict, purposefully modify and tune the quantum yield values of photoredox reactions.

The first rules of photoreactivity of complexes (the Adamson rules[19]) related the quantum yield of photosubstitutions to the spectral LF parameters of chromium(III) complexes. The rules, lately reelaborated, have a certain predictive value.

For photoredox reactions most results do not obey expectations based on a common chemical sense. This will be exemplified for two classes of compounds, the first being the complexes $[Co(NH_3)_5X]^{2+}$.

Irradiation of the aqueous systems containing the complexes $[Co(NH_3)_5X]^{2+}$ leads, depending on experimental conditions, along with photosubstitution reactions, to either an inner-sphere photoredox decomposition

$$[Co(NH_3)_5X]^{2+} \xrightarrow{h\nu} Co^{2+} + 5NH_5 + X^{\cdot}$$

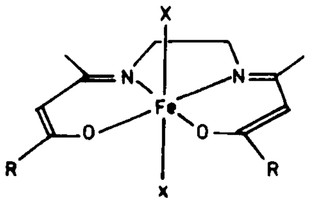
(the corresponding quantum yield being denoted as ϕ^{IS}) or an outer-sphere electron-transfer process within ion-pairs followed by a decomposition of the reduced complexes (the quantum yield denoted as ϕ^{OS})

$$[\mathrm{Co^{III}(NH_3)_5X}]^{2+}\cdot \mathrm{Y}^- \xrightarrow{h\nu} [\mathrm{Co^{II}(NH_3)_5X}]^+ + \mathrm{Y}^{\cdot},$$

$$[\mathrm{Co^{II}(NH_3)_5X}]^+ \longrightarrow \mathrm{Co}^{2+} + 5\mathrm{NH_3} + \mathrm{X}^-.$$

The quantum yield values of either photoredox reaction do not correlate with any of the relevant acidoligand X^- properties. For a comparison with ES reactivity parameters of Co(III) complexes the values of E^0(trans-$[\mathrm{Co(Me_6[14]4,11\text{-}dieneN_4)X_2}]^{+/0}$) are included (electrochemical reactions of the complexes are nearly reversible[17]) instead of those for $[\mathrm{Co(NH_3)_5X}]^{2+}$. Even for the outer-sphere electron-transfer processes (electrochemical and photochemical) there is no correlation between the E^0-values and ϕ^{OS}-values.

In our laboratory we have investigated photoredox properties of the complexes abbreviated as trans-$[\mathrm{Fe(L_{eq})X_2}]^{n+}$, where L_{eq} are tetradentate open-chain Schiff-base N_2O_2-ligands forming the equatorial plane of the complexes; X are monodentate ligands $\mathrm{CH_3COO^-}$, $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{NCS^-}$, $\mathrm{N_3^-}$ and $\mathrm{CH_3OH}$ bonded in axial positions. The shape of the complexes can be schematized as follows:



The complexes undergo a photoreduction of Fe(III) to Fe(II) when irradiated in methanol by ultraviolet light.[24–26] In the primary photoredox step the photoreduction of Fe(III) is associated with the photooxidation of a ligand X^-, the equatorial ligand L_{eq} being virtually chemically untouched:

$$[\mathrm{Fe^{III}(L_{eq})X_2}]^- \xrightarrow{h\nu} [\mathrm{Fe^{II}(L_{eq})X}]^- + \mathrm{X}^{\cdot}.$$

The overall chemical change (still for an anionic X^- ligand) in the systems can be expressed by a simplified stoichiometry

$$2[\mathrm{Fe^{III}}(\mathrm{L_{eq}})\mathrm{X_2}]^- + 3\mathrm{CH_3OH} \xrightarrow{h\nu} 2[\mathrm{Fe^{II}}(\mathrm{L_{eq}})(\mathrm{CH_3OH})_2]$$

$$+ 4\mathrm{X}^- + 2\mathrm{H}^+ + \mathrm{CH_2O}.$$

Some of the results obtained are gathered in Table II. Comparing the quantum yield values ϕ for the complexes possessing the same equatorial ligand L_{eq} and different redox reactive axial ligands X^- it is obvious that the ϕ values correlate neither with the $E^0(X^-/X)$ values nor with $x(X^-)$ and $I(X^-)$ values of the axial ligands ($E^0(\mathrm{CH_3COO^{\cdot}/CH_3COO^-}) = 1.92$ V; the related values for the other ligands are in Table I).

A similar conclusion concerns the relationships of the quantum yields ϕ and the Hammett or Taft parameters which can be taken as a measure of the electronic influence of the peripheral groups R of the equatorial ligands L_{eq} on the central atom Fe(III) and its bonds with the ligands X^-. Of the known substituent constants[27,28] those σ_H and σ_T showing the best correlations with the E^0-values for the complexes $[\mathrm{M}(\mathrm{L_{eq}})\mathrm{X_2}]^{n+}$, where M = Co, Cu, Fe and Ni[29–31] are included in Table II. Trying to find a reasonable correlation of the quantum yields with other substituent constants led to the same negative results.

Both the ligands X^- and the remote groups R influence the ability of the complexes to undergo photoredox reactions. We are not able, however, to quantify the impact of this influence on photoredox reactivity of complexes.

The reasons why there is not found any correlation between GS properties of complexes (their constituents) and the quantum yields of their photoredox decomposition can be, in general, classified into four groups:

(1) The central atom and ligands lose their original (usually free-molecular) GS properties upon bonding and excitation. The changes are different for each excited state and, in addition, they are not equal for all members of a homologic series of complexes.

(2) The lifetime of excited complexes is often very short (par-

TABLE II

Overall quantum yields $\phi(\lambda_{irr}$, nm) for photoredox reactions of the complexes trans-$[Fe(L_{eq})X_2]^{n+}$ in methanol; Hammett σ_H and Taft σ_T parameters of the peripheral groups R of the equatorial ligands L_{eq}.[24-26]

R	σ_H	σ_T	X^-	ϕ (254 nm)	ϕ (313 nm)
C_6H_4Br	0.26	0.83	CH_3COO^-	0.47	0.30
			Cl^-	1.33	0.11
			Br^-	0.071	0.060
			NCS^-	0.12	0.014
			N_3^-	-	0.050
			CH_3OH	-	0.041
C_6H_4Cl	0.22	0.83	CH_3COO^-	0.79	0.15
			Cl^-	1.07	0.042
			Br^-	0.031	0.11
			NCS^-	0.51	0.089
			N_3^-	-	0.043
			CH_3OH	-	0.039
C_6H_5	0.11	0.60	CH_3COO^-	0.47	0.14
			Cl^-	1.04	0.041
			Br^-	0.031	0.066
			NCS^-	0.91	0.39
			N_3^-	-	0.013
			CH_3OH	-	0.035
CH_3	-0.07	0.00	CH_3COO^-	0.33	0.11
			Cl^-	0.66	0.019
			Br^-	0.086	0.073
			NCS^-	0.84	0.41
			N_3^-	-	0.018
			CH_3OH	-	0.028
$C_6H_4CH_3$	-0.20	0.43	CH_3COO^-	0.51	0.39
			Cl^-	0.73	0.063
			Br^-	0.042	0.032
			NCS^-	0.49	0.22
			N_3^-	-	0.003
			CH_3OH	-	0.038
$C_6H_4OCH_3$	-0.67	0.33	CH_3COO^-	1.25	0.29
			Cl^-	1.06	0.094
			Br^-	0.066	0.022
			NCS^-	0.78	0.37
			N_3^-	-	0.029
			CH_3OH	-	0.032

ticularly for spin-allowed states) which prevents an efficient bimolecular photoreaction from occurring. It means that an excited complex itself may have a strong intrinsic tendency to undergo a bimolecular deactivation process but it is deactivated in a physical monomolecular mode before it collides with a possible reaction partner.

(3) Overall quantum yields are often negligible due to the fast recombinations of ground-state products formed in the primary photoredox step. The efficiency of such recombinations is driven thermodynamically: the more negative ΔG of the recombination, the higher its rate constant and efficiency. The second factor controlling the efficiency of recombinations is the kinetic energy of the primary photoproducts which is proportional to the difference of the photon energy and the treshold energy of the reaction. When the kinetic energy of the redox changed partners is low the recombination is favorable. If the kinetic energy is high the redox changed partners may diffuse apart and the probability of their recombination becomes lower.

(4) The kind of observed net photochemical reaction can differ from that of the primary photoredox step. For example, the radical $NO_2^{\cdot}$ produced by a photoredox decomposition of the nitroisomer $[Co(NH_3)_5NO_2]^{2+}$ is recoordinated through an oxygen atom forming nitritoisomer $[Co(NH_3)_5ONO]^{2+}$. Two redox reactions thus lead to a non-redox isomerization. Moreover, several chemical deactivations can simultaneously be realized in an irradiated system containing one light-absorbing species. As a classical example[16] again the complex $[Co(NH_3)_5NO_2]^{2+}$ can serve which, after having been excited, deactivates by two distinct redox processes, three different aquation reactions, and a linkage isomerization.

Current knowledge does not, unfortunately, allow us to utilize known GS characteristics of complexes for modeling their composition and structure in order to obtain just the required efficiency of their photoredox reactions. Consequently, keeping in mind practical needs, we are not able to optimize the photoredox behaviour of complexes. Based on the up-to-date knowledge of GS and ES chemistry a conclusion can be drawn stating that correlations between GS parameters of complexes and the quantum yield of their photoredox reactions have no theoretical background and are not justifiable.

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