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Energy Transfer Between Organic Molecules and Transition Metal Ions

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Modern ideas on radiationless energy transfer in solutions are described briefly. The fundamental formulae for the rates of this process, involving inductive-resonance and exchange-resonance mechanisms, are presented. Studies on the quenching of the fluorescent and triplet states of organic molecules by transition metal ions are surveyed and it is shown that in most cases radiationless energy transfer takes place.

Energy transfer from a fluorescent state to transition metal ions proceeds via a dipole - dipole mechanism and energy transfer from a triplet state involves an exchange-resonance mechanism. Studies on radiationless energy transfer between transition metal ions and molecular oxygen are also considered. The prospects for using energy transfer to elucidate the pathways and mechanisms of photochemical reactions of coordinated transition metal compounds in solutions are discussed.

The bibliography includes 110 references.

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I. MODERN IDEAS ABOUT THE MECHANISMS OF THE RADIATIONLESS TRANSFER OF ELECTRONIC EXCITATION ENERGY

In the last decade electronic energy transfer has found increasing applications in the solution of chemical, physical, and biological problems [1-6]. The method of triplet–triplet energy transfer between organic molecules, which is nowadays used in every other study on the mechanisms of photochemical reactions, constitutes the most striking example [1-4].

It has become evident in the last five years [7-9] that there exists yet another large chemical field where the application of energy transfer is extremely promising, namely the coordination chemistry of transition metal ions and lanthanide ions in solution. Radiationless energy transfer methods yield much information about the kinetics and mechanisms of the formation of complexes and photochemical reactions involving coordination compounds. In the present review attention is concentrated on the possibilities arising from the application of energy transfer in the study of interaction between transition metal ions and organic molecules in solution.

The radiationless transfer of electronic excitation energy in solution has been most thoroughly investigated for the interaction between two organic molecules [10,11]. The study of energy transfer from organic molecules to transition metal ions began only in the last few years. Since a review dealing with this field has not so far been published, the present survey is submitted to the reader.

Energy transfer in solution frequently proceeds via one of two fundamental mechanisms: inductive-resonance or exchange-resonance. In the inductive-resonance mechanism the interaction of an excited energy donor species with an unexcited acceptor species takes place via electromagnetic fields. Only interactions between electric dipole transitions in the donor and acceptor (dipole–dipole energy transfer) have so far been observed experimentally in solution. The theory of this type of energy transfer has been fairly thoroughly developed by Förster [10] and Galanin [11]. The expression defining the rate constant for energy transfer by this mechanism between a donor and an acceptor at a distance R is [12]

$$k_n(dd) = 8.8 \cdot 10^{-25} n^{-4} \tau_{0D}^{-1} q_{0D} R^{-6} \Phi^2 \int I_D^n(\nu)\, \varepsilon_A(\nu)\, \nu^{-4}\, d\nu \ (\text{in } s^{-1}), \quad (1)$$

where n is the refractive index of the solution, τ_{0D} and q_{0D} are the decay time and the luminescence quantum yield of the donor in the absence of the acceptor, Φ^2 is a coefficient which depends on the orientation of the dipole moments of the transitions in the donor and the acceptor ($\Phi = \cos\varphi_{D^*A} - 3\cos\varphi_{D^*}\cos\varphi_A$), [12-14] $I_D^n(\nu)$ the quantum intensity distribution in the luminescence spectrum of the donor normalised for a unit surface area, $\epsilon_A(\nu)$ the molar decadic extinction coefficient of the acceptor, and ν the wavenumber (cm^{-1}).

The expression for the critical radius of energy transfer (R_0) corresponding to the distance over which energy transfer and intramolecular deactivation are equally probable [i.e. $k_t(R_0) = \tau_{0D}^{-1}$] is:

$$R_0^6 = 8.8 \cdot 10^{-25} n^{-4} q_{0D} \Phi^2 \int I_D^n(\nu) \varepsilon_A(\nu) \nu^{-4} d\nu \ . \quad (2)$$

In the presence of sufficiently rapid molecular rotation the average value $\bar{\Phi} = \sqrt{2}/3$ in the calculation of R_0 for solid solutions by Eqn. (2) becomes $\bar{\Phi} = 0.845 \times \sqrt{2}/3$. [13,14] The phenomenon of singlet–singlet energy transfer between organic molecules, which has been thoroughly investigated, constitutes a typical example of dipole–dipole interaction [15].

The exchange-resonance mechanism of energy transfer becomes of primary importance when the radiative transitions in the donor and acceptor are forbidden by selection rules. Its occurrence requires an overlap of the electron clouds of the energy donor and acceptor. The formula describing the rate of transfer via the exchange-resonance mechanism is [16]

$$k_t(ex) = \frac{2\pi}{\hbar} Y \cdot e^{-\frac{2R}{L}} \int I_D^n(\nu)\, \varepsilon_A^n(\nu)\, d\nu \ , \quad (3)$$

where Y is a constant which cannot be determined from optical experiments, L is the average effective Bohr radius

characterising the rate of decrease of electron density in the peripherial regions of the interacting molecules (ions) of the energy donors and acceptors, and $I_D^n(\nu)$ and $\epsilon_D^n(\nu)$ are the emission spectrum of the donor and the absorption spectrum of the acceptor normalised for a unit surface area. The constant $k_t(ex)$ is also directly proportional in this case to the overlap integral of the normalised spectra and decreases exponentially with the distance between the donor and the acceptor. The exchange-resonance interactions are responsible for the triplet–triplet energy transfer between organic molecules [17].

Formulae for the laws governing the interaction in energy transfer via dipole–dipole (*dd*) and exchange-resonance (*ex*) mechanisms between individual molecules were given above. In a real experiment we do not observe these individual laws but the situation which arises as a result of the averaging of the interaction of unexcited acceptor molecules which have a random distribution in solution relative to the excited energy donor molecules. A number of studies have been devoted to mathematical models of the averaging, starting with those of Förster [10] and Galanin [11].

The following energy transfer parameters in solution are usually observed experimentally: (1) the decrease of the luminescence quantum yield of the energy donor as a function of acceptor concentration C_A: $q_{oD}/q_D = f(C_A)$; (2) the decrease of the average duration of donor luminescence as a function of acceptor concentration: $\bar{\tau}_{oD}/\bar{\tau}_D = f'(C_A)$; (3) the change in the donor luminescence decay law in the presence of the acceptor; (4) the change in these relations when the viscosity, temperature, solvent, and other parameters are varied; (5) the intensity (yield) of sensitised acceptor luminescence as a function of acceptor concentration: $q_{s.a.l.} = f''(C_A)$; (6) the sensitised acceptor luminescence excitation spectra, and many other parameters.

The concentration $(C_A)_e$ for which $q_{oD}/q_D = e$ can be determined from the variation of the degree of quenching of donor luminescence with acceptor concentration in solid (highly viscous) solutions. Hence the experimental critical energy transfer radius can be found† from the formula

$$R_0^{exp} = \frac{7{,}35}{\sqrt[3]{(C_A)_e}} \quad (R_0^{exp} \text{ in Å and } C_A \text{ on molar scale}). \tag{4}$$

Comparison of R_0^{exp} with R_0^{theor} calculated by Eqn. (2) makes it possible to reach a conclusion about the energy transfer mechanism. Another convenient parameter which depends on the transfer mechanism in solid (highly viscous) solutions is the ratio of the slopes of the curves

$$\rho = \lim_{C_A \to \infty} \left[\frac{d(q_D/q_{oD})}{dC_A} \Big/ \frac{d(\bar{\tau}_D/\bar{\tau}_{oD})}{dC_A} \right], \tag{5}$$

which is two for the dipole–dipole transfer, as shown correctly for the first time by Galanin [14]. Later a similar problem for other types of energy transfer was discussed by Sveshnikov and Shirokov [18] and Inokuti and Hirayama [19].

On passing to liquid solutions, it is necessary to take into account the mutual diffusion of donor and acceptor molecules during the lifetime of the excited state of the former. The presence of diffusion increases the degree of quenching of the donor in the presence of a specific concentration of the acceptor, provided that τ_{oD} remains unchanged on passing from a solid to a liquid solution. In the general case of random diffusion, its influence on energy transfer can be taken into account in terms of the theory developed by Rozman and coworkers [20], but only with the aid of computer calculations. An important new parameter in such calculations is the distance R_{min} of closest approach of the excited energy donor and the acceptor. The lack of accurate data for R_{min} may introduce the largest error into the calculations of the parameters of dipole–dipole energy transfer with allowance for diffusion. On the other hand, the marked dependence of energy transfer on R_{min} can yield valuable information about the immediate environment of the interacting species (the energy donor and acceptor). For steady-state excitation, the influence of the diffusion of the donor and acceptor on the energy transfer can be taken into account also by the method which was proposed by Bagdasar'yan and Muler [21]. Their tables make it possible to compare the experimental and theoretical data.

In very fluid (non-viscous) solvents the limiting case of "total mixing" in Galanin's terminology [11] may be attained. Under these conditions, the quenching of donor luminescence remains exponential at all the concentrations of the quenching agent and the decrease of the donor luminescence yield and τ in the presence of the acceptor is the same in each case ($q_{oD}/q_D = \tau_{oD}/\tau_D$) and is a linear function of the acceptor concentration. Tunitskii and Bagdasar'yan [22] showed that the quenching rate constant in this limiting case of "infinite diffusion coefficients" is related by a simple mathematical expression to the critical energy transfer radius and the distance of closest approach:

$$k_t^{theor} = \frac{4}{3}\pi N' \frac{R_0^s}{R_{min}^s} \cdot \frac{1}{\tau_{oD}} \text{ (litre mole}^{-1}\text{ s}^{-1}\text{)}, \tag{6}$$

where $N' = 10^{-3}N$ and N is the Avogadro number. Eqn. (6) is in fact the same as the formula derived earlier by Galanin and Frank [23] using the classical model for energy transfer from an emitting dipole to a continuous absorbing medium. The condition for the applicability of Eqn. (6) is

$$\sqrt{\gamma'/\sigma} \ll 1, \text{ where } \gamma' = \left(\frac{R_0}{R_{min}}\right)^6; \ \sigma = \frac{D\tau_{oD}}{R_{min}^2},$$

$D = D_D + D_A$ is the sum of the diffusion coefficients of the donor and acceptor.

The exponential quenching of donor luminescence and the linearity of the relation $q_{oD}/q_D = \tau_{oD}/\tau_D = \text{const.} C_A$ are maintained also for $(R_0^2/D\tau_0)^{3/2} \ll 1$; alternatively we have approximately $\bar{r} = \sqrt{2D\tau_{oD}} > R_0$, i.e. when the mean square displacement ($\bar{r}$) during the lifetime of the excited state of the donor exceeds severalfold the critical energy transfer radius R_0. On the other hand, for large values of R_0 the last condition cannot correspond to the case of "total mixing" and Eqn. (6) becomes invalid. A fairly complex mathematical expression for k_t under these conditions was derived by Tunitskii [24]. The $D^{3/4}$ law discovered by Yokota and Tanimoto [25] is a special case when $1 \ll 5(D\tau_{oD}/R_0^2)^3 \ll (D\tau_{oD}/R_{min}^2)^2$. Then k_t^{theor} is also described by the simple expression

$$k_t^{theor} = 2\pi^{3/2} N' D^{3/4} R_0^{3/2} \tau_{oD}^{-1/4}. \tag{7}$$

All the above considerations refer to energy transfer between electrically neutral species. However, in many cases the energy donor and acceptor exist in solution as electrically charged species: anions or cations. Thus the theory of radiationless energy transfer must take into account the electrostatic interactions between the energy donor and acceptor and the deviations caused by them from the random distribution of acceptor species around

† In a dipole–dipole energy transfer the concentration $(C_A)_e$, determined from the change of q_D, corresponds to $(C_A)_2$, i.e. to twofold quenching determined from the decrease of τ_D. [19]

the excited donor. This theory was developed by Bodunov[26-28] in terms of the *dd* approximation for solid and liquid solutions. As a result of the electrostatic interaction between the donor and acceptor, the acceptor concentration as a function of the distance from the donor becomes:

$$C_A(r) = C'_A \cdot \exp(-U(r)/kT),$$

where C'_A is the acceptor concentration far from the excited donor and $U(r)$ the electrostatic interaction energy between ions. It has been assumed[26] that $U(r)$ is determined by shielded Coulombic interaction. In his later studies Bodunov[27,28] found the interaction energy as the exact solution of the Poisson equation for the electrostatic potential generated by D* in an electrically neutral solution.

It was shown in the above studies that the effect of electrostatic interaction on *dd* energy transfer for ions bearing charges of the same sign is significant mainly in liquid solutions alone. In solid solutions the contribution of these interactions does not exceed 10–20% and therefore cannot be detected experimentally. For ions bearing charges of different sign, this influence can be manifested also in the absence of diffusion-controlled processes in the solution. The dependence of energy transfer on the electrostatic interaction between ions is determined by many factors, the main ones of which are the dielectric constant of the solvent ϵ and the distance of closest approach between the ions R_{min} (for ions having different charges). For $C_A > C_D$, electrostatic interactions can lead to a curvature (in consequence of the shielding effect of the acceptor molecules) of the relations between q_{0D}/q_D and C_A. The form of this curvature depends on whether the energy donor and acceptor have the same or different charges. The shielding or suppression of electrostatic interaction can also be achieved by adding extraneous electrolytes to the solution.

The number of studies dealing with the theory of analogous problems in relation to the exchange-resonance type of energy transfer is significantly smaller[19]. It has been shown that in a highly viscous solution the energy donor luminescence quantum yield should decrease much faster than the average decay time of donor luminescence. The experimental discrepancy between the ratios q_{0D}/q_D and $\bar{\tau}_{0D}/\bar{\tau}_D$ makes it possible to estimate the average effective Bohr radius L in Eqn.(3).[19] In liquid solutions the exchange-resonance energy transfer obeys in most cases the same relations as other "fast" chemical reactions involving excited species, for example electron transfer reactions and other collision-controlled processes[29,30].

Thus the determination of the rate constants for energy transfer reactions, the ratio of the decrease of the donor luminescence yield to τ, the law governing the decay of donor luminescence in the presence of an acceptor, and the variation of the energy transfer characteristics with the concentrations of the components, the solvent, and the spectral characteristics of the interacting species makes it possible to establish the mechanism of the energy transfer in each specific case. In many instances it is possible to obtain information from energy transfer data about the existence of short-lived unstable complexes, which cannot be detected by other methods.

Below we shall attempt to arrange systematically experimental data which throw light on the mechanism of the interaction in the quenching by transition metal ions of the excited singlet and triplet states of organic molecules and of singlet oxygen. Data concerning the influence of the structure of these molecules and complexes and also of the solvent on the quenching rate constants will be considered. In addition, we shall discuss the applications of energy transfer in the study of the mechanisms of photochemical reactions of transition metal complexes of different types.

II. THE MECHANISM OF THE QUENCHING OF THE FLUORESCENCE OF ORGANIC COMPOUNDS BY TRANSITION METAL IONS

The quenching of the fluorescence of organic compounds by transition metal ions in solution has been known for a long time[31,32], but its mechanism still remains not altogether clear. Weiss[33] rejected the idea that such quenching is related to the intersystem crossing catalysed by the paramagnetism of the quenching agents on the grounds that many paramagnetic ions (for example Mn^{2+}) do not quench the fluorescence of dyes. Linschitz and Pekkarinen[34] also observed only very weak quenching effects due to Mn^{2+} and Zn^{2+} ions. To explain the quenching of the fluorescence of organic molecules by transition metal ions, Terenin[35] and later Linschitz and Pekkarinen[34] proposed a reversible charge transfer mechanism. The latter workers[34] noted a parallelism between the quenching efficiencies for fluorescence and for the triplet state[34,36-38]. However, sufficiently convincing experimental results establishing a relation between the degree of quenching and the redox potentials of the cations were not quoted.

Another concept was put forward by Galanin and Lëvshin[39]. They attributed the pronounced quenching of the fluorescence of quinine sulphate and 3-aminophthalimide by Cr^{3+} in glycerol to inductive-resonance energy transfer from these organic molecules to Cr^{3+}. There is at present a growing interest in the mechanism of the processes involved in the quenching of the fluorescence of organic compounds by transition metal ions. This is related mainly to the recent observation of the sensitising action of organic molecules on photochemical reactions of transition metal complexes. Naphthalene sensitises the photochemical reduction of $[Co(NH_3)_6]^{3+}$ to Co^{2+}.[40] The Stern–Volmer fluorescence quenching (200 litre mole^{-1}) and sensitisation (170 litre mole^{-1}) constants proved to be closely similar in this instance. The quinolinium ion also sensitises this reaction[41] via the excited triplet state (k_T = 36.6 litre mole^{-1}). In the sensitised photochemical reduction of $[Co(Phen)_3]^{3+}$ the fluorescence of free *o*-phenanthroline (Phen) is quenched by the complex[42] with k_T = 600 litre mole^{-1}. The sensitised photochemical aquation of the complex $[Cr(NH_3)_5X]^{2+}$, where X^- = Cl^- or NCS^-, i.e. $[Cr(NH_3)_5X]^{2+} \rightarrow [Cr(NH_3)_4(H_2O)X]^{2+} + NH_3$, has been investigated in solutions containing acridinium ions[43] and riboflavine[44]. The simultaneous quenching of the fluorescence of the latter was observed. The fluorescence of naphthalene is quenched when it sensitises the photochemical reaction of $[Cr(CN)_6]^{3-}$.[45]

Varnes et al.[46] studied the effect of 13 metal ions on the fluorescence of riboflavine. The decrease of the fluorescence yield on quenching is consistent with the decrease of its τ and obeys a linear relation. With increase of temperature, k_T rises, while an increase in viscosity causes its diminution. However, the results obtained do not yield clear-cut conclusions concerning the mechanism of the quenching of fluorescence.

We attempted to revise the above data[40,43,44,46] as well as the results of earlier studies by Weber[47,48] from the standpoint of energy transfer via the dipole (*dd*) mechanism. Table 1 presents the experimental k_T from the

above studies, and our calculated overlap integrals of the spectra (J_0), the critical energy transfer radii (R_0^{theor}), and the theoretical energy transfer rate constants (k_t^{theor}). The k_t^{theor} were calculated by Eqn. (6) assuming infinite diffusion coefficients and $R_{min} = 8$ Å.

Table 1. The quenching of the fluorescence of organic compounds by transition metal ions.

Donor	Transition metal ion	$10^{-9}k_q$, litre mole^{-1} s^{-1}	$10^{17} \times J_0$,	$10^{26}k_q/J_0$	R_0, Å	$10^{-9}k_t^{theor}$ litre mole^{-1} s^{-1}
Naphthalene* (H_2O + EtOH (1 : 1); 293 K $\tau_{fl}^0 \cong 1$ ns, $q_{fl}^0 \cong 10^{-1}$] (Ref.40)	$[Co(NH_3)_4]^{3+}$	~20	5,1	—	10	~5 ~12 (R_{min}=6Å)
Acridinium ion (H_2O + 0.1 *N* H_2SO_4; 298 K τ_{fl}^0 = 43 ns, q_{fl}^0 = 0.77) (Ref.43)	$[Cr(NH_3)_5NCS]^{2+}$	6.0	32	—	18,9	5,3
Riboflavine (H_2O, pH 3.2; 298 K)(Ref.44)	$[Cr(NH_3)_5NCS]^{2+}$	4,2	17	0,25	14,1	6,2
	$[Cr(NH_3)_5Cl]^{2+}$	5,2	18	0,29	14,3	6,7
Riboflavine (H_2O, pH 2.6; 303 K: τ_{fl}^0 = 4.7 ns; q_{fl}^0 = 0.75) (Ref.46)	V^{3+}	4,6	3,7	1,2	11,0	1,8
	Cr^{3+}	3,6	8,4	0,4	12,6	3,6
	Co^{2+}	3,2	1,7	1,9	9,6	0,83
	Cu^{2+}	1,2	0,32	3,8	7,3	0,16
	Ni^{2+}	0,55	0,24	2,3	6,9	0,12
	Mn^{2+}	<0,04	0,03	<1,3	4,9	0,015
	Zn^{2+}, Ba^{2+}, Pb^{2+}	<0,04	0,00	—	—	—
	Fe^{2+}	3,6	0,08	45	—	—
Quinine sulphate** (H_2O + 1 *N* H_2SO_4; 293 K; $\tau_{fl}^0 \cong 20.1$ ns, q_{fl}^0 = 0.54) (Refs.47,48)	Cr^{3+}	7,5	3,8	2,0	12,5	0,94
	Co^{2+}	2,3	1,8	1,3	11,1	0,45
	VO^{2+}	0,50	0,68	0,7	9,4	0,17
	Ni^{2+}	0,26	0,54	0,5	9,0	0,13
	Cu^{2+}	0,17	0,13	1,3	7,1	0,032
	Mn^{2+}	0,023	0,01	2,3	4,8	0,003
	Fe^{2+}	1,3	0,02	650	—	—

*τ_{fl}^0 and q_{fl}^0 were estimated by the present authors.
**The values of k_q for this compound were estimated by the present authors from the literature data [47,48] on the assumption that the Stern–Volmer relation between q_0/q and C_A holds and that $\tau_{fl}^0 \simeq 20.1$ ns.

We established that the error for $\sigma/\gamma' > 1.5$ arising from the use of this formula does not exceed 10% of the overall error. For systems comprising riboflavine and $[Cr(NH_3)_5X]^{2+}$ (with $X^- = NCS^-$ or Cl^-), $[Cr(H_2O)_6]^{3+}$, and $[V(H_2O)_6]^{3+}$, where $\sigma/\gamma' < 1.5$, calculations of k_t^{theor} were made on a computer by the method of Rozman and coworkers [49] using $D \simeq 1 \times 10^{-5}$ cm^2 s^{-1}.

Examination of the data in Table 1 leads to the following conclusions: (1) in most cases there is a satisfactory correlation between k_q and J_0 (except for the Fe^{2+} ion); (2) the experimental quenching rate constants (k_q) are appreciably greater (by a factor of 2–8) than the calculated rate constants for energy transfer via the *dd* mechanism (k_t^{theor}).

In many instances the differences between the above quantities are small and can be entirely due to the inaccuracy of the parameter R_{min}. If the energy donor is charged, one must also consider the influence of the electrostatic interaction of the ions on the fluorescence quenching process.

Thus the parallel variation of k_q and overlap integrals of the spectra and the agreement within an order of magnitude between k_q^{exp} and k_t^{theor}, estimated from the formulae for *dd* energy transfer, demonstrate convincingly that the radiationless energy transfer from excited singlet states of organic compounds to transition metal ions is one of the most likely processes responsible for quenching when the fluorescence spectra overlap with the absorption spectra of transition metal ions.

The marked discrepancy between k_q^{exp} and k_t^{theor} for Fe^{2+} is probably due to the fact that the reversible electron transfer to the excited molecule of the organic compound with formation of Fe^{3+} via Terenin's mechanism [35] is dominant under these conditions.

III. THE MECHANISM OF ENERGY TRANSFER FROM TRIPLET STATES OF ORGANIC MOLECULES TO TRANSITION METAL IONS

1. SOLID SOLUTIONS

The mechanism of the quenching of the phosphorescence of organic compounds by transition metal ions has also been inadequately elucidated. In the first studies by Pankeeva [50,51], carried out in solid solutions of ethanol and acetic and formic acid at 90 K, it was postulated that the transition metal ions exhibit a paramagnetic effect on the phosphorescence, i.e. they initiate a radiationless intercombination transition from the triplet to the ground state. She studied the quenching of the phosphorescence of fluorescein and trypaflavine by Ni^{2+}, Mn^{2+}, and Fe^{3+} ions and found that the relations between q_D/q_{oD} and τ_D/τ_{oD} on the one hand and the transition metal concentration on the other differ markedly and the two ratios vary exponentially with the concentration of quenching agents. Smaller et al. [52] studied by ESR the quenching of the phosphorescence of perdeuterionaphthalene (naphthalene-d_8) in a 9 : 1 mixture of methanol and water at 77 K by Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Fe^{3+}, and Gd^{3+} ions. They discovered a non-rigorous proportionality between the rate of such quenching and the magnetic moments (in Bohr magnetons) of the transition metal ions, which they regarded as supporting a mechanism of paramagnetic influence of the quenching agents (for a criticism of this study, see below).

Hill and Lin [53,54] used Hoijtink's idea [55,56] about the involvement of exchange interactions in the postulated quenching of the triplet state of organic molecules catalysed by paramagnetic transition metal ions. They compared the experimental parameters of the quenching of the naphthalene-d_8 phosphorescence in ethanol by Co^{2+}, Cr^{3+}, Cu^{2+}, and Ni^{2+} ions (at 77 K) with the theoretical values calculated on the basis of the above model. They were the first to note the non-exponential quenching of the phosphorescence in the presence of paramagnetic substances in addition to the discrepancy between the variations of q_D/q_{oD} and τ_D/τ_{oD} with the concentration of such substances.

Best agreement between theory and experiment was achieved for the parameters γ and C_A^0 quoted in Table 2. The diamagnetic Zn^{2+} ion does not quench the phosphorescence up to $C = 0.25$ M. The experimental data [53,54] do not confirm the exchange mechanism for the interaction of naphthalene with transition metal ions. Thus there are considerable variations in C_A^0 in the series of these ions; it is unlikely that the overlapping of electron clouds of

different transition metal ions and naphthalene-d_8 varies quite so much. The values of R_0^{exp} for the above systems are large, i.e. they exceed considerably the sum of the radii of both components. Table 2 also presents the ratios ρ of the limiting slopes of the degree of quenching–concentration curves, which were calculated by Eqn.(5) from determinations [53,54] of the changes in q_{0D} and τ_{0D}. The Table shows that the ratios are in the range 0.50 to 0.57, i.e. are a characteristic of the dipole–dipole energy transfer.

Table 2. The quenching of the phosphorescence of organic compounds by aquated transition metal ions in solution at 77 K.

Donor	Transition metal ions	R_0^{exp*}, A	ρ	C_A^0, M	ν
Naphthalene-d_8 in 95% ethanol (Refs.53,54)	Co^{2+}	12.4	0.50	0.210	4.4
	Cr^{3+}	24.3	~0.55	0.028	10.0
	Cu^{2+}	17.8	~0.50	0.072	12.0
	Ni^{2+}	11.0	0.57	0.298	7.0
Naphthalene-d_8 in 9:1 methanol–water mixture (Ref.57)	Co^{2+}	14.3**	0.52		
	Ni^{2+}	13.4	0.24		
	Mn^{2+}	14.6	0.13		
Triphenylene in 9:1 methanol–water mixture (Ref.57)	Co^{2+}	15.5**	0.50		
	Ni^{2+}	14.4	0.12		
	Mn^{2+}	14.9	0.10		

*The values of R_0^{exp} were obtained [53,54] on the assumption of an exchange interaction and from the condition of best agreement between the experimental and theoretical values of C_A^0. In another study [57] the R_0^{exp} were obtained from the exponential relations between q_D/q_{0D} and C_A within the framework of the model postulating a limited sphere of quenching action.
**On the assumption of dipole–dipole interaction.

The most clear-cut data were obtained in a recent study by Breuninger and Weller [57], who investigated the quenching of the phosphorescence of triphenylene and naphthalene-d_8 by Co^{2+}, Ni^{2+}, and Mn^{2+} ions. The authors treat the observed quenching of the phosphorescence as a radiationless energy transfer from the triplet states of the molecules with excitation of the transition metal ions. The parameters ρ discussed above [see Eqn.(5)] were calculated in the same study [57] (Table 2). $\rho = 0.50-0.52$ for Co^{2+}, which supports the dipole–dipole mechanism of the interaction. For the remaining ions, the parameter ρ is much smaller (about 0.1–0.2) and much closer to the values for exchange interaction [19]. In the naphthalene-d_8–Ni^{2+} system ($\rho = 0.24$) both types of interaction are postulated. Table 2 also lists the values of R_0^{exp}, which exceed somewhat the R_0 for the triplet–triplet energy transfer [17]. The latter finding is incomprehensible. The reason for the small difference between the R_0^{exp} for the dipole–dipole (transfer to Co^{2+}) and exchange (Mn^{2+}, Ni^{2+}) transfer mechanisms deduced from the parameters ρ is also obscure.

Breuninger and Weller [57] showed that the reduction of the intensity of the ESR signal of the naphthalene-d_8 triplet state by paramagnetic transition metal ions, observed by Smaller et al. [26], is due to the broadening of the ESR lines in the presence of the paramagnetic ions, which increases with the magnetic moment of the ion.

2. LIQUID SOLUTIONS

The quenching of the fluorescence of organic molecules in the triplet state by transition metal ions in liquid solutions was observed in 1958 simultaneously by Porter and Wright [37,38] and by Linschitz and Sarkaninen [36]. In the first investigations [36–38] it was suggested that the quenching is due to the radiationless transition of organic molecules to the ground state catalysed by paramagnetic transition metal ions in accordance with the scheme

$$^3D + {}^nM_j^{k+} \rightarrow {}^1D + {}^nM_j^{k+}, \quad n \geqslant 2 \qquad (8)$$

or due to reversible electron transfer reactions:

$$^3D + {}^nM_j^{k+} \rightarrow {}^2D^+ + {}^mM_i^{(k-1)+}, \qquad (9a)$$

$$^3D + {}^nM_j^{k+} \rightarrow {}^2D^- + {}^mM_i^{(k+1)+}, \qquad (9b)$$

where ^3D is the organic molecule in the triplet state, $^2D^+$ and $^2D^-$ are the radical-cation and radical-anion derived from this molecule, and $^nM_j^{k+}$ is the transition metal ion.

Below we shall attempt to show that the most effective process involved in the quenching of triplet molecules of organic compounds by transition metal ions in liquid and solid solutions is radiationless energy transfer. Most of the studies published on this problem in recent years tend to support this view [58–62]. It is noteworthy that the quenching of the triplet state by transition metal ions in solutions is more closely related to chemical interactions than the quenching of fluorescence. The exchange-resonance mechanism of the process responsible for the "physical" quenching in this case requires the overlapping of the electron clouds of the interacting molecules, which is necessary also for the formation of chemical bonds. However, there is no doubt that the existing relation between complex formation and the quenching of triplet molecules by a transition metal ion has so far been traced less distinctly than in the quenching by lanthanide ions [7–9]. Possibly this is related to the lack of systematic studies on this problem.

a. Direct Evidence for Energy Transfer

The sensitised luminescence of transition metal ions,

$$^3D^* + {}^nM_j^{k+} \xrightarrow{k_t} {}^1D + ({}^mM_i^{k+})^*,$$

$$({}^mM_i^{k+})^* \overset{k_R}{\rightsquigarrow} ({}^lM_k^{k+})^* \xrightarrow{k_{em}} {}^nM_j^{k+} + h\nu_{s.l.}, \qquad (10)$$

where $^nM_j^{k+}$, $(^mM_i^{k+})^*$, and $(^lM_k^{k+})^*$ is the complex of the transition metal ion in the non-excited, excited Franck–Condon, and excited resonance states from which emission takes place, constitutes direct evidence for radiationless energy transfer between the triplet molecule and transition metal ions. The sensitised luminescence of transition metal ions was observed experimentally for the first time by Binet et al. [58] They observed the simultaneous quenching of the phosphorescence of benzil‡ and the appearance of the sensitised phosphorescence of the complexes $[Cr(NCS)_6]^{3-}$ and $[Cr(CN)_6]^{3-}$ in a deoxygenated mixture of methanol and water at 160 K (Table 3). Anthracene ($^3\Gamma = 14\,950$ cm^{-1}) also sensitises the phosphorescence of chromium(III) complexes at 160 K in the above mixture [58] and at room temperature in dimethylformamide

‡ The fluorescence of benzil is not appreciably quenched under the experimental conditions by complex chromium(III) ions.

(DMF) [59]§. On freezing the solutions, the quenching and intensity of the sensitised phosphorescence were sharply reduced. The rate constants for energy transfer (k_t) estimated from the decrease of the benzil phosphorescence yield, the decrease of its phosphorescence decay time, and the increase in the intensity of the sensitised phosphorescence of chromium(III) complexes with increase of their concentration are listed in Table 3. Their scatter is small, except for $[Cr(NCS)_6]^{3-}$, where the differences are appreciable. It has been suggested [58] that the maximum value of k_t is close to the rate constant for the diffusion of the solvent under the experimental conditions, although viscosity measurements were not made.

Table 3. The rate constants for energy transfer from triplet benzil molecules ($^3\Gamma$ = 18 800 cm^{-1}, τ_0 = 1.5 ms) to chromium(III) complexes in an 88 : 12 methanol–water mixture at 160°C in the absence of molecular oxygen [58].

Acceptor	$10^{-6}k_t$, litre mole^{-1} s^{-1}	^2E_g, cm^{-1}	$^4T_{2g}$, cm^{-1}
$[Cr(NCS)_6]^{3-}$	5÷18	12 900	17 800
$[Cr(acac)_3]$	10	12 800	18 400
$[Cr(urea)_6]^{3+}$	2.8	14 240	16 300
$[Cr(CN)_6]^{3-}$	1.2÷4.0	12 500	26 700
$[Cr(en)_3]^{3+}$	1.3±0.3	15 000	21 900

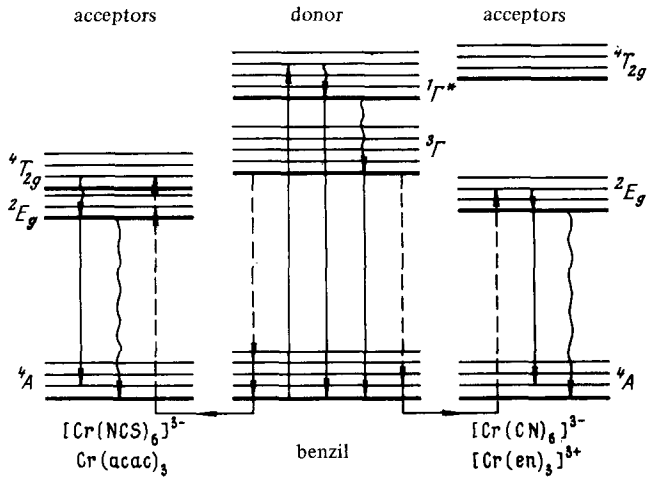


Figure 1. *Schematic illustration of the electronic levels in energy transfer from organic molecules (benzil) in the triplet state ($^3\Gamma$) to chromium(III) ions.*

If the complex with urea is excluded, then the following observation may be made for the remaining chromium(III) complexes listed in Table 3. The constant k_t decreases abruptly severalfold on passing from complexes where energy transfer to the ^2E_g and $^4T_{2g}$ levels is possible to complexes where energy may be transferred from the benzil triplet level only to the ^2E_g level of Cr^{3+} (Fig. 1).

§ Recently Balzani et al. [60] observed the phosphorescence of $[Cr(en)_3]^{3+}$ sensitised by diacetyl in water at 288 K.

Later Ohno and Kato [61] observed the phosphorescence of chromium(III) complexes sensitised by benzil and erythrosine. They noted that chromium(III) complexes quench effectively the phosphorescence of erythrosine but not its fluorescence. The admission of oxygen does not affect the phosphorescence of Cr^{3+} on direct excitation but fully suppresses its sensitised luminescence. The rate constants for energy transfer from erythrosine to chromium(III) complexes are listed in Table 4. Ohno and Kato [61] attribute the differences between the constants k_t to the aromatic or nonaromatic nature of the ligands in the complexes. However, we believe that the data in Table 4 clearly demonstrate a dependence of k_t on the charge of the complex ion: the higher the negative charge of the complex the smaller the value of k_t¶. This can be understood, since the energy donor (erythrosine) is in all probability present in solution as the dianion.

Table 4. The rate constants for the quenching of the triplet state of erythrosine ($^3\Gamma \simeq$ 14 800 cm^{-1}) in 9 : 1 ethanol–water mixture at 201 K in the absence of molecular oxygen [61].

Acceptor	$10^{-6}k_t$, litre mole^{-1} s^{-1}	^2E_g, cm^{-1}	$^4T_{2g}$, cm^{-1}	$^3\Gamma_{lig}$, cm^{-1}
Cr(oxine)$_3$	48	~13 100		~16 000
Cr(acac)$_3$	12	12 800	18 400	25 400
$[Cr(NCS)_4(aniline)_2]^-$	12	~13 100		~25 000
$[Cr(NCS)_4(NH_3)_2]^-$	6.2	13 300		>25 000
$[Cr(NCS)_6]^{3-}$	1.6	12 900	17 800	>25 000

Ohno and Kato's claim [61] that the constant k_t for energy transfer from erythrosine to $[Cr(oxine)_3]$ is equal to the diffusion constant is not altogether correct. The transfer from the excited triplet state of the ligand is indeed endothermic in this case (Table 4)†, but the rate of the triplet–triplet energy transfer is then usually lower than the diffusion rate [63].

A second fairly direct piece of evidence showing that the transfer of electronic excitation energy is in fact usually responsible for the quenching of the triplet state of organic molecules by transition metal ions is the sharp decrease of the quenching rate constant (k_t) when the lower excited resonance level of the transition metal ion in the complex lies above the triplet level, i.e. the energy transfer becomes endothermic. We were able to select from the literature a fairly large number of examples illustrating this postulate. They are presented in Table 5. These data constitute yet another significant confirmation that the quenching of the triplet molecules of organic compounds is caused by radiationless energy transfer.

¶ The chromium(III) and cobalt(III) complexes remain unchanged in solution for a long time, since the rate of exchange of their ligands with the solvent is very low: for example, the rate of thermal exchange between chromium(III) complexes and water is of the order of 10^{-6} s^{-1}. [64]

† The data for the $^3\Gamma$ level of erythrosine listed in Table 1 of Ohno and Kato's paper [61] are erroneous, since they are inconsistent with the Fig. 4 of the same communication and other literature data.

Although the mechanism of the induced catalysis of intersystem crossing in accordance with Eqn.(8), proposed in early investigations [37,38], is in fact possible in the above instances, its probability is lower. Table 5 shows that the rate constants for this process have an upper limit $\leq(0.1-1)\times10^6$ litre mole^{-1} s^{-1}, which is 1–3 orders of magnitude lower than the rate constants for the energy transfer.

Table 5. The effect of the relative energies of the triplet states of organic molecules and the excited resonance levels of transition metal ions on the rate constants for the quenching of triplet states in solution at 293 K.

Donor	$^3\Gamma_D$, cm^{-1}	Complex*	E_{res}, cm^{-1}	$10^{-6}k_t$, litre mole^{-1} s^{-1}	Solvent	Refs.
Anthracene	14 950	$[Cr(H_2O)_3Cl_3]$	—	200	THF + H_2O	34
ditto	14 950	$[Ni(H_2O)_6]^{2+}$	8 500	160		34
»	14 950	$[Co(H_2O)_6]^{2+}$	8 000	210		34
»	14 950	$[Cu(H_2O)_6]^{2+}$	~9 400	320		34
»	14 950	$[Mn(H_2O)_6]^{2+}$	~19 000	1,3		34
Tetraphenyl-porphin	13 000**	$[Ni(Py)_6]^{2+}$	~8 000—10 000	10	Pyridine	34
	13 000	$[Mn(Py)_6]^{2+}$	18 000—20 000	<0.5		34
Acridine	15 840	$[Cr(C_2O_4)_3]^{3-}$	14 350	610	H_2O	62
ditto	15 840	$[Co(H_2O)_6]^{2+}$	8 000	10		62
»	15 840	$[Cr(OH)_6]^{3-}$	~17 200	<1		62
»	15 840	$[Mn(H_2O)_6]^{2+}$	~19 000	<1		62
Triphenylene	23 500	$[Cr(CN)_6]^{3-}$	12 500	9,7	EtOH + THMF** + H_2O	66
Chrysene	20 000	$[Cr(CN)_6]^{3-}$	12 500	27		66
Anthracene	14 950	$[Cr(CN)_6]^{3-}$	12 500	59		66
Ditto	14 950	$[Cr(en)_3]^{3+}$	15 000	11		66
Naphthacene	10 300	$[Cr(CN)_6]^{3-}$	12 500	<0,2		66

*All the symbols used for the ligands in the complexes here and henceforth are consistent with the generally accepted notation (see, for example, the monograph of Basolo and Pearson [64]).

**According to the data of Gradyushko et al. [65]

***THMF = tetrahydro-2-methylfuran.

An analogy can be drawn with complexes of lanthanide ions. The triplet state of the tris-β-dibenzoylmethanate ($^3\Gamma_{lig}\simeq20\,500$ cm^{-1}) of La^{3+} (a diamagnetic ion) has a quenching time $\tau_0=0.5$ s for the phosphorescence in an organic glass at 77 K. When La^{3+} is replaced by the paramagnetic Gd^{3+} ion with a high resonance level ($^6P_{7/2}=32\,000$ cm^{-1}), τ_0 for the ligand decreases to 2×10^{-3} s. [67] On the other hand, τ_0 for the triplet level of the ligand decreases sharply on passing to lanthanide ion complexes with a resonance level below the $^3\Gamma_{lig}$ level of, for example, Eu^{3+} ($^5D_0\simeq17\,200$ cm^{-1}) and Sm^{3+} ($^4G_{5/2}\simeq17\,800$ cm^{-1}). The lifetime of the triplet state of the organic ligand in complexes of this type is shown by the rate of energy transfer to lanthanide ions, to be about 10^{-9} s or less [68,69].

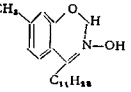
Direct experiments permitting an unambiguous choice between the hypotheses concerning the energy transfer and the catalysis of intercombination transitions as the causes of the quenching of triplet molecules by transition metal ions were described by Allsopp and Wilkinson [70], who showed that the planar diamagnetic nickel(II) and palladium(II) complexes with Schiff bases effectively quench the triplet states of molecules whose triplet level lies above the excited states of transition metal ions in the ligand field (about 2500 cm^{-1} for Ni^{2+} and 16 500 cm^{-1} for Pd^{2+}; see Table 7) but are below the triplet level of the ligand ($^3\Gamma_{lig}\simeq21\,000$ cm^{-1}). Since the above complexes have a singlet ground state, the possibility of the mechanism involving the spin catalysis of intercombination transitions in accordance with Eqn.(8) is completely ruled out; the only remaining possibility is that these complexes quench via the mechanism involving the heavy atom effect.

Table 6. Effect of the structure of the transition metal complex on the rate of exothermic energy transfer from triplet aromatic hydrocarbon molecules in liquid solutions at 293 K.

Donor	$^3\Gamma$, cm^{-1}	Acceptor	Solvent	$10^{-6}k_t$, s^{-1} litre mole^{-1}	Refs.
Triphenylene	23 500	$[Cr(CN)_6]^{3-}$	H_2O + THMF + EtOH (29:1:70)	9,7	65
ditto	23 500	$[Cr(SCN)_4(NH_3)_2]$		340	65
»	23 500	$[Cr(OC(NH_2)_2)_6]^{3+}$		36	65
Naphthalene	21 250	$[Cr(H_2O)_6]^{3+}$	H_2O	69	34, 38
ditto	21 250	$[Co(H_2O)_6]^{2+}$		50	34, 38
»	21 250	$[Mn(H_2O)_6]^{2+}$		28	34, 38
»	21 250	$[Fe(H_2O)_6]^{3+}$		29	34, 38
»	21 250	$[Cu(H_2O)_6]^{2+}$		75	34, 38
»	21 250	$[Ni(H_2O)_6]^{2+}$		23	34, 38
»	21 250	$[Co(H_2O)_6]^{2+}$		90	34, 38
»	21 250	$[Cr(NH_3)_6]^{3+}$	H_2O+EtOH (1:1)	33	73
»	21 250	$[Cr(NH_3)_5Cl]^{2+}$		200	73
Chrysene	20 000	$[Cr(CN)_6]^{3-}$	H_2O + THMF + EtOH(33:7:60)	27	66
ditto	20 000	$[Cr(en)_3]^{3+}$		62	66
»	20 000	$[Cr(en)_2Cl_2]^+$		200	66
»	20 000	$[Cr(NH_3)_5Cl]^{2+}$		200	66
»	20 000	$[Cr(OC(NH_2)_2)_6]^{3+}$		560	66
»	20 000	$[Cr(SCN)_4(NH_3)_2]^-$		1300	66
Anthracene	14 950	$[Cr(CN)_6]^{3-}$	H_2O+EtOH (3:7)	59	66
ditto	14 950	$[Cr(OC(NH_2)_2)_6]^{3+}$		5,7	66
»	14 950	$[Cr(en)_3]^{3+}$		11	66
»	14 950	$[Cr(NH_3)_5Cl]^{2+}$		30	66
»	14 950	$[Cr(SCN)_4(NH_3)_2]^-$		560	66

Table 7. The rate constants for exothermic energy transfer from triplet molecules to transition metal complexes with aromatic ligands in benzene at room temperature.

Donor	$^3\Gamma$, cm^{-1}	Acceptor	$10^{-9}k_t$, litre mole^{-1} s^{-1}	Refs.
Phenanthrene	21 700	$Fe(acac)_3$	3.3	75
Naphthalene	21 250	$Fe(acac)_3$	1.8	75
Anthracene	14 950	$Fe(acac)_3$	0.7	75
»	14 950	$Cr(acac)_3$	1.3	75
»	14 950	$Cu(acac)_2$	0.6	75
»	14 950	$Cu(dpm)_2$	0.3	75
»	14 950	$Ni^{II}(SB)_2$(planar)	2.6÷4.3	76
»	14 950	$Ni^{II}(SB)_2$(tetr.)	<0.01	76
Chrysene	20 000	Ni^{II}(Hen-Sam-OH)(oct.)	<0.2	76
Benzophenone	24 200	$Fe(dpm)_3$	0.9	77
1-Naphthaldehyde	19 750	$Fe(acac)_3$	2.7	77
	19 750	$Fe(dpm)_3$	0.9	77
2-Acenaphthone	20 800	$Fe(acac)_3$	1.9	75
»	20 800	$Cu(acac)_3$	1.9	75
»	20 800	$Cu(dpm)_3$	0.5	75
Benzil	18 800	$Fe(acac)_3$	2.7	75
»	18 800	$Cr(acac)_3$	1.1	75
Fluorenone	18 650	$Cr(acac)_3$	1.2	75
Diacetyl	19 000	$Fe(acac)_3$	3.1	78
Benzophenone	24 200	$Pd(SB)_2$(planar)	3.0	72
Chrysene	20 000	ditto	2.3	72
1,2,3,4-Dibenzanthracene	17 800	»	1.4	72
Pyrene	16 900	»	<0.05	72
Acridine	15 800	»	<0.05	72
Anthracene	14 950	»	<0.05	72

Notation: dpm = dipivalomethanate; SB = Schiff bases with different substituents; tetr. = tetrahedral; oct. = octahedral; Hen-sam-OH = 

b. Effect of the Structure of the Organic Molecule and the Transition Metal Complex and of the Properties of the Solvent on the Rate of Energy Transfer

After the discovery of the method of flash photolysis of Norrish and Porter [71,72], numerous studies were published in which the rate constants for the quenching of triplet molecules by transition metal ions were determined by this procedure. As shown above, in most cases the quenching is due to energy transfer.

Table 6 presents the constants k_t for the transfer of triplet energy from aromatic hydrocarbons at room temperature. It shows that in most cases k_t is around 10^7-10^8 litre mole^{-1} s^{-1}, which exceeds by 1–3 orders of magnitude the analogous constant for the transfer of triplet energy from aromatic hydrocarbons to lanthanide ions [1,7,8,34,38]. The constant k_t increases by a further order of magnitude (to 10^9 litre mole^{-1} s^{-1}) in the quenching of triplet molecules by complexes of transition metal ions with aromatic ligands, as can be seen from the data in Table 7. The quenching is not associated with energy transfer to the triplet level of the ligand, because transfer processes of the latter type are strongly endothermic under the experimental conditions. Table 7 shows that the energy transfer to complexes with aromatic ligands is independent of the structure of the energy donor molecules, in particular of the presence in the latter of active carbonyl and other groups. This shows that the exchange-resonance interactions between the π system of the triplet molecule and the d shell of the transition metal ion takes place effectively via the π system of the coupled ligand. Steric hindrance to the mutual approach of the organic molecule and the π-electron system of the chelate, arising on passing from acetylacetonates to dipivalomethanates, leads to a decrease of k_t by a factor of 2–4 (Table 7).

Table 8. The rate constants for the quenching of triplet naphthalene molecules by transition metal ions in solvents of different viscosities at 293 K in the absence of molecular oxygen [38].

Quenching agent-acceptor	Solvent I and k_d	$10^{-7}k_t^I$, litre mole^{-1} s^{-1}	Solvent II and k_d	$10^{-7}k_t^{II}$, litre mole^{-1} s^{-1}
$[Ni(H_2O)_6]^{2+}$	Water ($k_d = 6.5\cdot10^9$ litre mole^{-1} s^{-1})	2.3	Ethylene glycol ($k_d = 3\cdot10^8$ litre mole^{-1} s^{-1})	2.3
$[Co(H_2O)_6]^{2+}$		5.0		4.4
$[Mn(H_2O)_6]^{2+}$		2.8		1.6
$[Cu(H_2O)_6]^{2+}$		7.5		7.3

The influence of the ligand on the quenching activity of copper(II) chloride has also been studied [77]. The authors observed that ethylenediamine used as a ligand decreases while *o*-phenanthroline increases the rate of quenching of the triplet state of anthracene.

The effect of complex formation on the quenching of triplet anthracene by Co^{2+}, Ni^{2+}, and Cu^{2+} ions in ethylene glycol at 298 K was studied by Yatsimirskii and Dagaev [79–81]. It was shown that the formation of complexes by the above ions with ethylenediamine, ethylenediaminetetra-acetate, diethylenetriaminepenta-acetate, and cyclohexanediaminetetra-acetate increases the quenching rate constant by a factor of 2–4.

It is at present impossible to reach definite conclusions about the effect of the structure of the complexes and the organic molecules on the rate of energy transfer, since none of the scientific schools have carried out systematic studies on this problem.

The problem of the effect of the solvent on the efficiency of energy transfer from triplet molecules to transition metal ions has also been little investigated. Nevertheless we believe that some data on this problem can be usefully mentioned. Since the rate constants k_t for energy transfer to transition metal complexes with non-aromatic ligands are lower by 1–3 orders of magnitude than the diffusion rate constants k_d, an increase in the viscosity of the solvent should not have an appreciable effect on k_t until k_d becomes smaller than k_t in solvents with a low viscosity. The data of Porter and Wright [38] quoted in Table 8 constitute an experimental confirmation of this conclusion. Evidently the change in viscosity by a factor of 20 on passing from water to ethylene glycol hardly affects k_t. One should bear in mind that an increase in the viscosity of the solvent usually leads to a simultaneous increase of the lifetime of the triplet molecules and is accompanied by an increase in the quantum yield of the energy transfer reaction‡ φ_t at the same energy acceptor concentration. Hence it is possible to increase φ_t by increasing the viscosity of the solvent—by changing it for a related solvent or by reducing the temperature. Admittedly the latter is possible only when the transfer process lacks an appreciable activation energy.

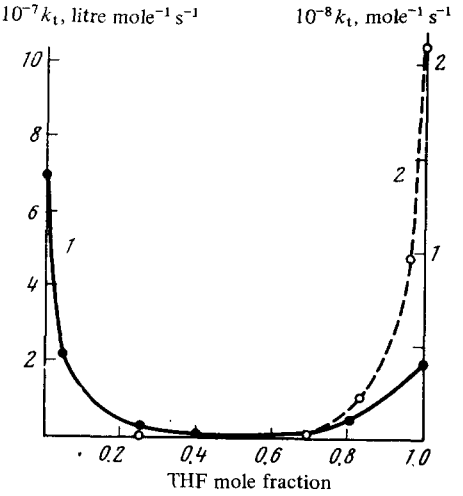


Figure 2. Dependence of the rate constant for the quenching of the triplet state (k_t) of naphthalene by cobalt(II) chloride (curve *1*) and of anthracene by cobalt(II) perchlorate (curve *2*) on the composition of the solvent (water–tetrahydrofuran) [34,73].

Although the rate of energy transfer from triplet molecules to transition metal ions was measured in different solvents (see Tables 3–8), it is at present difficult to

‡ We interpret the quantum yield of the energy reaction φ_t as the ratio of the number of transfer steps to the number of donor triplet molecules formed during the same period under quasisteady-state conditions.

reach any definite conclusions about the role of the chemical nature of the solvent in this process. However, one should note an early study by Linschitz and Pekkarinen [34] in which it was shown that k_t for energy transfer from anthracene and tetraphenylporphin triplets to transition metal ions in tetrahydrofuran and pyridine decreases by 1–3 orders of magnitude after the addition of water to the solvent (Fig. 2). On the other hand, Rogov et al. [73] recently investigated the influence of the addition of alcohols or ethers (Fig. 2) on the rate constant for energy transfer from naphthalene triplet to cobalt(II) complexes. Fig. 2 shows that k_t falls in this case too. There is at present no unambiguous explanation of this interesting phenomenon. Possibly effects associated with the ordering of the solvent molecules in the second coordination sphere of the transition metal ion play a significant role here.

IV. ENERGY TRANSFER BETWEEN TRANSITION METAL COMPLEXES AND MOLECULAR OXYGEN

Studies by Farmilo and Wilkinson [82] and Carlson et al. [83] have now firmly established that transition metal complexes are effective quenching agents for singlet molecular oxygen in solution. It has been shown that the quenching constants are independent of the method of preparation of singlet oxygen. The value of τ for singlet molecular oxygen was estimated by analysing the kinetics of the disappearance of the absorption of 1,3-diphenylazobenzofuran or rubrene in its presence.

Table 9. The constants for the quenching of singlet oxygen by transition metal ions in various solvents at 298 K according to the literature [82,83].

Quenching agent	Solvent	$10^{-8}k_t$, litre mole^{-1} s^{-1}
$Ni^{II}(SB)_2$	Benzene	30
$Pd^{II}(SB)_2$	Benzene	0.6
Di-(2-hydroxy-5-methoxyphenyl-N-n-butylaldimine)-nickel(II)	Iso-octane	35
	Hexadecane	2.0
Nickel(II) di-n-butyldithiocarbamate	Iso-octane	7.0
	Hexadecane	9.0
Nickel(II) n-butylamine[2,2'-thiodi-(4-t-octyl)-phenoxide]	Iso-octane	1.8–2.7
	Hexadecane	0.8
Nickel(II) acetylacetonate	Iso-octane	1.3–2.0
Nickel(II) di(*O*-butyl-3,5-di-t-butyl-4-hydroxybenzyl-phosphonate)	2-Butoxyethanol	0.34
$NiCl_2.6H_2O$	"	3.1
$CoCl_2.6H_2O$	"	0.48
$MnCl_2.4H_2O$	"	<0.01

Table 9 presents the constants for the quenching of singlet oxygen by complexes of different transition metals. The most effective quenching agents are nickel(II) complexes, whose resonance state lies below or possible in some cases at the same energy as O_2 ($^1\Delta g$). The efficiency of quenching by many nickel(II) complexes depends significantly on the ligand. The highest constants are observed for nickel(II) complexes with Schiff bases (SB). The complex $[Mn(H_2O)_6]^{2+}$, the excited resonance state of which is higher than the $^1\Delta g$ state of oxygen, does not quench singlet oxygen. Presumably the main process involved in the quenching of singlet oxygen by transition metal ions is, as for triplet organic molecules, radiationless transfer of electronic excitation energy, which proceeds via an exchange-resonance mechanism, bearing in mind that the $^1\Delta g \rightarrow {}^3\Sigma\bar{g}$ electronic transition in oxygen is forbidden.

Table 10. The rate constants for the quenching of the luminescence of chromium(III) complexes by oxygen extrapolated to 298 K (in the 2 : 1 : 1 mixture of methanol, water, and ethylene glycol as solvent) [84].

Energy donor	$10^{-9}k_t$, litre mole^{-1} s^{-1}	Energy donor	$10^{-9}k_t$, litre mole^{-1} s^{-1}
$[Cr(acac)_3]$	100**	$[Cr(CN)_6]^{3-}$	0.2
$[Cr(NCS)_6]^{3-}$	6	$[Cr(en)_3]^{3+}$	<0.01
$\{trans\text{-}Cr(NH_3)_2(NSC)_4\}^{1-}$	2	$[Cr(tmen)_3]^{3+}$ *	<0.01

*tmen = trimethylethylenediamine.

**The values of k_t for $Cr(acac)_3$ at 298 K is unreliable, since it was found by extrapolating to 298 K the values of k_t measured below 180 K.

The quenching of the phosphorescence of excited chromium(II) complexes by molecular oxygen was observed and studied by Pfeil [84]. He assumed that the quenching mechanism involves exchange-resonance energy transfer and explains the marked dependence of the rate constant for the quenching of the phosphorescence of the complexes by oxygen on the nature of the ligand in the complex (Table 10) by the different capacities of the ligands to conduct π electrons and hence by the different overlapping of the electron clouds of the energy donor and acceptor. However, comparison of the data in Table 10 with those in Table 6 makes it clear that σ-binding ligands such as NH_3 or ethylenediamine (en) do not prevent energy transfer from organic molecules to transition metal complexes. We believe that, in discussing the involvement of the ligand in energy transfer between complexes and O_2, one must take into account the possibility of the formation of unstable transition metal complexes with O_2 and the effect of this process on the energy transfer. Transition metals are known to exhibit a tendency to form complexes with O_2. [85]

V. APPLICATIONS OF RADIATIONLESS ENERGY TRANSFER IN THE STUDY OF PHOTOCHEMICAL REACTIONS OF COORDINATION COMPOUNDS OF TRANSITION METAL IONS

The photochemistry of the coordination compounds of transition metal ions has developed very vigorously in recent years. Starting with the pioneer study by Volger and Adamson [86] (1968), the method of radiationless energy transfer from organic molecules began to be used in the investigation of the mechanisms of photochemical reactions. The largest number of studies have been devoted to chromium(III) and cobalt(III) complexes, since the mechanisms of the direct photochemical reactions of such complexes have been investigated in greatest detail. Investigations dealing with certain other ions have also begun to appear in recent years. Brief reviews of the mechanisms of photosensitised reactions are contained in an excellent monograph on the photochemistry of coordination compounds by Balzani and Carassiti [87] and also in other surveys [88–91]. However, they are already obsolete owing to the vigorous development of this field.

1. THE ROLE OF ENERGY TRANSFER IN DETERMINING THE REACTIVITIES OF THE LOWEST EXCITED STATES OF TRANSITION METAL COMPLEXES

The spectroscopy of transition metal complexes has shown that, depending on the strength of the ligand field, the long-wavelength absorption band of the complexes may correspond both to a transition allowed by the spin selection rules and to a forbidden intercombination transition. In the latter case direct selective population of the lowest excited level of the complex by light is difficult, since it is impossible to separate the weak intercombination absorption from the stronger allowed absorption of the adjacent band. In many instances the application of radiationless energy transfer helps in overcoming these difficulties.

It can now be regarded as firmly established that organic molecules are capable of sensitising photochemical reactions of transition metal complexes by energy transfer both from excited singlet [43,44,46] and triplet [92] states.

The processes (for example photochemical aquation processes) occurring in a binary solution {organic sensitiser—energy donor (D) and the transition metal complex $[M^{k+}L_l]$} can be represented schematically as follows (it is assumed that under the experimental conditions the intrinsic absorption of the complex can be neglected compared with the absorption of the sensitiser):

Scheme I

$$^1D + h\nu \rightarrow {}^1D^*, \quad (I\text{-}1)$$

$$^1D^* + {}^nM^{k+}L_l \rightarrow {}^1D + {}^nM^{k+}L_l{}^*, \quad k_{ts}\ (I\text{-}2)$$

$$^nM^{k+}L_l{}^* + H_2O \rightarrow M^{k+}L_{l-1}H_2O + L, \quad k_R(I\text{-}3)$$

$$^1D^* \rightarrow {}^1D + h\nu_{fl}, \quad k_{em}(I\text{-}4)$$

$$^1D^* \rightsquigarrow {}^3D, \quad k_{i.r.}(I\text{-}5)$$

$$^3D + {}^nM^{k+}L_l \rightarrow {}^1D + {}^mM^{k+}L_l{}^*, \quad k^I_{tT}(I\text{-}6)$$

$$^mM^{k+}L_l{}^* + H_2O \rightarrow M^{k+}L_{l-1}H_2O + L, \quad k^I_R(I\text{-}7)$$

$$^3D + {}^nM^{k+}L_l \rightarrow {}^1D + {}^nM^{k+}L_l{}^*, \quad k^{II}_{tT}(I\text{-}8)$$

$$^nM^{k+}L_l{}^* + H_2O \rightarrow M^{k+}L_{l-1}H_2O + L, \quad k^{II}_R(I\text{-}9)$$

$$^3D \rightsquigarrow {}^1D, \quad k_D\ (I\text{-}10)$$

where ^1D and ^3D are the singlet and triplet states of the sensitiser, M^{k+} is the transition metal ion, L is the ligand, n and m are the multiplicities of the states of the complex, and an asterisk designates electronically excited states.

Whether the photochemical reaction occurs via the singlet or triplet sensitisation channel depends on the ratios of the probabilities of all the processes involving the given excited state of the donor.

It is known from the energy transfer theory that, for effective energy transfer from the donor to the acceptor, two requirements must be met: an energy requirement—the level of the energy donor must lie above the level of the acceptor (the overlapping of the emission spectrum of the donor and the absorption spectrum of the acceptor must be a maximum)—and a spin requirement. For maximum efficiency of the inductive-resonance energy transfer from the excited singlet level of the donor, it is necessary that the multiplicities of the excited and ground states should be identical both in the donor molecule and in the acceptor complex; for exchange-resonance energy transfer, it is necessary that Wigner's rule (the overall spin of the system must remain unchanged) should hold for the transfer process.

The sensitisation of photochemical reactions of transition metal complexes by energy transfer from the excited singlet state of the organic molecule [40] is not of much interest for the elucidation of the mechanisms of such reactions, since it is equivalent (see Scheme I) to direct excitation of the complex in the region of its allowed absorption band.

The study of the dependence of the reactions of the complexes on the height of the triplet level of the sensitiser makes it possible in many instances to reach an unambiguous conclusion about the inertness or reactivity of the lowest excited states of transition metal complexes, i.e. about the energies of the photochemical activated states of non-phosphorescent complexes§.

We shall consider separately two different cases of energy transfer to transition metal complexes.

1. Transfer to low-spin complexes with a set of singlet and triplet energy states. In particular, cobalt(III), rhodium(III), and platinum(II) [94] complexes have zero spin in the ground state. In this case, according to Wigner's rule, of the two processes 6 and 8 in Scheme I only process 6, i.e. triplet–triplet energy transfer to these complexes, is allowed. Consequently the very fact that a sensitised photochemical reaction occurs in this case is unambiguous evidence for the reactivity of the triplet state of the complex. The involvement of the triplet states of the complexes $[Co(CN)_6]^{3-}$, $[Co(CN)_5X]^{2-}$ (where X = Br, Cl, I, or pyridine) [95,96], $[Rh(NH_3)_5X]^{2+}$ (where X = Br, Cl, or I), [92] and $[PtCl]^{2-}$ [97] in their photochemical aquation reactions was demonstrated by this method. In all these studies diacetyl was used as the sensitiser. The quenching of its phosphorescence in the presence of the complexes and the constant intensity of its fluorescence lead to the unambiguous conclusion that the triplet state of diacetyl is responsible for the sensitisation.

2. The transfer of triplet excitation energy to all stable low- and high-spin transition metal complexes with any set of multiplet states other than that considered in paragraph 1 above. In this case both energy transfer processes (processes 6 and 8 in Scheme I) are possible, according to Wigner's rule, for exchange-resonance energy transfer.

If the energy gap between the two lowest excited levels of the transition metal ion is fairly large (>2400 cm^{-1}, see Moggi and Balzani [90]), the reactivity of the lowest excited state of the ion can be determined by studying the dependence of the sensitisation of the photochemical reaction on the height of the triplet level of the sensitiser. This method was used in the investigation of the relative reactivities of the doublet and quartet states of chromium(III) complexes. Diacetyl, acridine, Michler's ketone, and Methylene Blue were used as sensitisers for the complex $[Cr(NH_3)_5NCS]^{2+}$; [43] $[Cr(CN)_6]^{3-}$ was sensitised by pyrazine, xanthone, Michler's ketone, anthracene, and $[Ru(bipy)_3]^{2+}$. [59,98] Among these sensitisers, diacetyl, acridine, pyrazine, and xanthone, i.e. the compounds whose triplet level lies above the $^4T_{2g}$ level of Cr^{3+}¶ show the greatest ability to induce the photochemical aquation of the chromium(III) complexes. This result indicates the photochemical activity of the $^4T_{2g}$ level of Cr^{3+}. The demonstration of the low probability of the aquation reaction via the ^2E_g level follows from a comparison of the

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§ Only a few transition metal complexes are phosphorescent in liquid solutions [93].

¶ The failure of Michler's ketone, whose triplet level is also above the $^4T_{2g}$ level, to cause sensitisation is probably due to the short lifetime of its triplet state in solution, i.e. $k_{tT}[M] < \tau_3^{-1}$.

data for the ability of anthracene and the complex $[Ru(bipy)_3]^{2+}$ to sensitise the phosphorescence of $[Cr(CN)_6]^{3-}$ in dimethylformamide at a reduced temperature with data concerning the absence of the photosensitised photochemical aquation reaction in the systems $[Ru(bipy)_3]^{2+}$ (sensitiser)$-[Cr(CN)_6]^{3-}$ in water and anthracene$-[Cr(CN)_6]^{3-}$ in dimethylformamide. All the considerations adduced here for the photochemical aquation reaction are equally valid for the photochemical isomerisation of transition metal complexes.

The situation is more complex in the sensitisation of the photochemical reduction reaction, for example the photochemical reduction of the amino-complexes of cobalt(III) which takes place on excitation of the triplet states of diacetyl, biphenyl, and quinoline[41,99]. Together with energy transfer and subsequent reduction of cobalt from the tervalent to the bivalent state in the complex itself (see process 1 in Scheme II), type 2 electron transfer is also possible in this system.

Scheme II

$$^3D + [Co(NH_3)_6]^{3+} \rightarrow {}^1D + {}^3([Co(NH_3)_6]^{3+})^* \xrightarrow{+\text{solv.}} {}^1D + [Co(NH_3)_6]^{2+}, \quad (II-1)$$

$$^3D + [Co(NH_3)_6]^{3+} \rightarrow {}^2D^+ + [Co(NH_3)_6]^{2+} \xrightarrow{+\text{solv.}} {}^1D + [Co(NH_3)_6]^{3+}. \quad (II-2)$$

Unambiguous information about the reactivities of the different levels of the cobalt(III) complex can be obtained after eliminating process (II–2). For each specific system, the problem of the relative rates of energy and electron transfer requires special consideration. The same difficulty arises in attempts to investigate the photochemical reduction of Fe^{3+} by the energy transfer method.

2. THE QUANTUM YIELDS OF SENSITISED PHOTOCHEMICAL REACTIONS

Additional information about the pathways followed in photochemical reactions and the probabilities of intercombination transitions in complexes is provided by a comparison of the quantum yields of photochemical reactions in direct photolysis (φ_{ph}^{dir}) and in the sensitisation of the lowest excited state of the complex (φ_{ph}^{sens}).

We shall consider the photochemical aquation reaction.

It is again necessary to deal separately with complexes which have a singlet ground state. For such complexes, the quantum yield of the photochemical aquation reaction in direct excitation $\varphi_{aq}^{dir} = q_{^3\Gamma}(K)\Phi_{aq}(^3\Gamma) + \Phi_{aq}(^1\Gamma^*)$, where $q_{^3\Gamma}(K)$ is the quantum yield in the formation of the triplet state of the complex, $\Phi_{aq}(^3\Gamma)$ the quantum yield in the aquation of the triplet state, and $\Phi_{aq}(^1\Gamma^*)$ the quantum yield in the aquation of the singlet excited state of the complex. Under the conditions of total transfer via triplet levels from the organic sensitiser to the complex, the quantum yield of the sensitised photochemical aquation reaction $\Phi_{aq}^{sens} = q_{^3\Gamma}(D)\Phi_{aq}(^3\Gamma)$, where $q_{^3\Gamma}(D)$ is the quantum yield for the formation of the sensitiser triplets.

In this case comparison of φ_{aq}^{dir} with $\varphi_{aq}^{sens} q_{^3\Gamma}^{-1}(D)$ permits definite conclusions concerning the mechanism of the photochemical process: (1) when $\varphi_{aq}^{dir} = \varphi_{aq}^{sens} q_{^3\Gamma}^{-1}(D)$, then presumably the triplet state of the complex is the only reactive state and $q_{^3\Gamma}(K) = 1$; the alternative hypothesis that $\Phi_{aq}(^1\Gamma^*) = \Phi_{aq}(^3\Gamma)$ is less probable; the yields of the direct and diacetyl-sensitised reactions were found to be the same for the rhodium(III), platinum(II), and cobalt(III) complexes of the type $[Rh(NH_3)_5X]^{2+}$ (X = Cl^-, Br^-, or I^-),[92] $[Co(CN)_5Y]^{2-}$ (Y^- = N_3^-, NCS^-, or CN^-),[95] and $[PtCl_4]^{2-}$;[97] (2) when $\varphi_{aq}^{dir} < \varphi_{aq}^{sens} q_{^3\Gamma}^{-1}(D)$, it follows that $q_{^3\Gamma}(K) \leq \varphi_{aq}^{dir}/\varphi_{aq}^{sens} q_{^3\Gamma}^{-1}(D)$. Assuming that the reaction proceeds only via the triplet state of the complex $[\Phi_{aq}(^1\Gamma^*) = 0]$, it is possible to obtain $q_{^3\Gamma}(K)$ by comparing the yields of the direct and sensitised reactions. Such estimates of $q_{^3\Gamma}(K)$ have been made for $[Co(CN)_6]^{3-}$ [95] and $[PtCl_4]^{2-}$.[97] However, the data of Scandola and Scandola[95] conflict with the results of measurements of Wrighton et al.[96] (Table 11). (3) When $\varphi_{aq}^{dir} > \varphi_{aq}^{sens}$, the implication is that the singlet excited state of the complex is actively involved in the photochemical aquation process and $\Phi_{aq}(^1\Gamma^*) > \Phi_{aq}(^3\Gamma)$.

Among the transition metal complexes which do not have a singlet ground state, chromium(III) compounds were investigated in greatest detail. It was already noted above

Table 11. Comparison of the quantum yields of the direct and sensitised (by energy transfer from the triplet state of organic molecules) photochemical aquation reactions of transition metal complexes.

Complex $[M^{III}X_nY_m]$	Medium	Region of direct excitation	φ_{aq}^{dir} for different substituents		Sensitiser	φ_{aq}^{sens} for different substituents		References
			X	Y		X	Y	
$[Cr(NH_3)_6]^{3+}$	H_2O + EtOH (1:1), 298 °K, 0.03*N* $HClO_4$	$^4T_{2g} \leftarrow {}^4A_{2g}$	0.24		Naphthalene	0.18		76
$[Cr(NH_3)_5Cl]^{2+}$	ditto	ditto	0.35		ditto	0.34		76
$[Cr(NH_3)_5NCS]^{2+}$	H_2O + 0.1 *N* H_2SO_4, Ar, 298 °K	»	0.21	$9.5\cdot10^{-4}$	Diacetyl	0.21	$<10^{-4}$	43
$[Cr(en)_3]^{3+}$	H_2O + (0.003 *N* $HClO_4$), 218 °K	»	0.4	—	ditto	0.8	—	60
$[Co(CN)_6]^{3-}$	H_2O, evacuated soln.	$^1T_{1g} \rightarrow {}^1A_{1g}$	0.31	—	»	0.23	—	96
$[Co(CN)_6]^{3-}$	ditto	ditto	0.31	—	»	0.80	—	95
$[Co(CN)_5N_3]^{3-}$	»	»		0.23	»	—	0.22	96
$[Co(CN)_5NCS]^{3-}$	»	»		0.2	»	—	0.18	96
$[Rh(NH_3)_5Cl]^{2+}$	H_2O (0.002*M* $HClO_4$), Ar, 298 °K	$^1T_1 \leftarrow {}^1A_1$	$<10^{-3}$	0.15	»	$<10^{-3}$	0.16	92
$[Rh(NH_3)_5Br]^{2+}$	»	^1E, $^1A_2 \leftarrow {}^1A_1$	0.18	0.019	»	0.20	0.02	92
$[Rh(NH_3)_5I]^{2+}$	»	$^1E \leftarrow {}^1A_1$	0.86	0.01	»	0.90	—	92
trans-$[Rh(NH_3)_4I_2]^{1+}$	»	$^1T_1 \leftarrow {}^1A_1$	—	0.48	»	—	0.59	92

X = NH_3, en, CN^-

that sensitisation via energy transfer from singlet levels with excitation of the quartet levels of chromium(III) is equivalent to direct excitation and measurement of the quantum yields of photochemical aquation in this case provides no new information about the relative reactivities of the ^2E_g and $^4T_{2g}$ levels of the complex. The observed difference between the yields of the direct and riboflavine-sensitised photochemical aquation of $[Cr(NH_3)_5Cl]^{2+}$ [44] conflicts with data of a study [101] where it was shown that the photochemical aquation quantum yield is independent of the exciting light wavelength and an investigation [43] where the values of φ_{aq}^{sens} and φ_{aq}^{dir} were found to be the same in sensitisation by the acridinium ion.

The quantum yields of the photochemical aquation of chromium(III) complexes with sensitisation via the triplet state of organic molecules were measured in a series of studies [43,60,76,102]. In this case

$$\varphi_{aq}^{sens} = \frac{k_{tT}^{II}}{k_{tT}^{I} + k_{tT}^{II}} \Phi_{aq}\ (^4T_{2g}) + \frac{k_{tT}^{I}}{k_{tT}^{I} + k_{tT}^{II}} \Phi_{aq}\ (^2E_g),$$

where k_{tT}^{I} and k_{tT}^{II} are rate constants for energy transfer from triplets with excitation of the doublets and quartets respectively (see Scheme I).

The presence of so many unknowns precludes a conclusion concerning the reactivities of the $^4T_{2g}$ and ^2E_g states on the basis of data for φ_{aq}^{sens} and φ_{aq}^{dir}. Possibly some information about the reactivities of mixed transition metal complexes can be provided by a study of the dependence of the composition of the products of the reaction of these complexes on λ_{exc}. Martin and Adamson [43] observed differences between the products of the photolysis of $[Cr(NH_3)_5NCS]^{2+}$ with excitation in the region of the $^4T_{2g}$ and ^2E_g bands.

Comparison of the photochemical reaction products of this salt for sensitisation with acridinium ions and diacetyl confirmed qualitatively the differences between the reactivities of the $^4T_{2g}$ and ^2E_g states observed in direct photolysis by light corresponding to the absorption bands for these states (Table 11). The authors conclude that the $^4T_{2g}$ and ^2E_g states are responsible for the photochemical aquation of the NH_3 and NCS^- groups respectively†.

A defect of this and many other studies quoted here is the lack of data for the intensity of the exciting light. On the other hand, the ratios of the rates of the photochemical reaction and the dark forward and reverse reaction depend on the intensity of the exciting light. Since the dark reaction of $[Cr(NH_3)_5(NCS)]^{2+}$ involves the displacement of NCS^- and the photochemical reaction involves predominantly the displacement of NH_3, the ratio of the reaction products should depend on I_{exc}.

3. THE QUENCHING OF THE PHOTOCHEMICAL REACTIONS OF TRANSITION METAL COMPLEXES BY ENERGY TRANSFER FROM THE LATTER

The method of suppressing a photochemical reaction by the introduction of a quenching agent supplements the sensitisation method. Its employment makes it possible to determine the position of the photochemically active state. The combination of the sensitisation and quenching methods yields information about the distortions of this state on excitation. For example, in the absence of sensitisation the *cis–trans* isomerisation of diglycinato-platinum(II) by organic molecules with a triplet state below 22 900 cm^{-1} and the absence of the quenching of the photochemical reaction of Pt^{2+} by Mn_{aq}^{2+} ions (18 900 cm^{-1}), while Ni_{aq}^{2+} ions do cause quenching (8900 cm^{-1})‡ provide information about the shift of the triplet state of platinum(II) on excitation [104].

The quenching method also makes it possible to estimate the contribution of the given state of the overall yields of the photochemical reaction of the complex. As for sensitisation, this method is particularly simple only for transition metal complexes with a set of singlet and triplet levels. In this case the method is analogous to the procedure involving the quenching of the triplet state of organic molecules [2-4].

For other sets of states, the method of quenching the photochemical reactions of transition metal ions by the molecular triplet states is again coupled with the difficulty of separating the processes involving energy transfer from the two lowest excited states of the transition metal ion. The closeness of τ_{fl} and τ_{phosph} for chromium(III) complexes at room temperature aggravates this difficulty still further. For the chromium(III) complexes which phosphoresce in liquid solutions, comparison of data for the influence of quenching agents on photochemical aquation and the phosphorescence of the complexes helps in obviating these difficulties. The employment of this method made it possible to study the pathways in the photochemical reaction of the Reinecke salt in various solvents at reduced temperatures {O_2 [101] and $[Cr(CN)_6]^{3-}$ [81] were used as quenching agents} and in the photochemical aquation of $[Cr(en)_3]^{3+}$ in water at 293 K [cobalt(II) and iron(II) salts served as the quenching agents [105]].

In order to determine the reactivities of the ^2E_g and $^4T_{2g}$ levels of chromium(III), data for the quenching of the phosphorescence of the Reinecke salt and $[Cr(en)_3]^{3+}$, the decrease of the duration of their phosphorescence, and the excitation of the sensitised phosphorescence of $[Cr(CN)_6]^{3-}$ were compared [101,105] with data for the suppression of their photochemical aquation in the presence of quenching agents. It was found that φ_{ph} changes in the presence of $[Cr(CN)_6]^{3-}$ or Ni^{2+} to a lesser extent than q_{phosph} and τ_{phosph} for the Reinecke salt and the complex $[Cr(en)_3]^{3+}$. The incomplete suppression of the photochemical aquation reaction on depopulation of the ^2E_g level of these salts by energy transfer to $[Cr(CN)_6]^{3-}$ is significant evidence in support of the photochemical activity of the $^4T_{2g}$ level of these chromium(III) complexes.

The high reactivity of the $^4T_{2g}$ level of hexacyanochromium(III) was demonstrated by Wasgestian [59], who investigated the effect of O_2 on τ_{phosph} and φ_{aq}^{dir} for the complex $[Cr(CN)_6]^{3-}$ in dimethylformamide at room temperature a and observed that τ_{phosph} for the solution decreases by a factor of 10 after evacuation, but the latter has no influence on φ_{aq}^{dir} for this complex. This result enabled him to claim that the ^2E_g state of $[Cr(CN)_6]^{3-}$ is not reactive. It is still not known whether this claim is true for all chromium(III) complex and whether the hypothesis of Porter et

† No difference in φ_{aq}^{dir} on excitation to the ^2E_g and $^4T_{2g}$ states were noted for the complexes $[Cr(en)_3]^{3+}$, $[Cr(NH_3)_6]^{3+}$, and $[Cr(urea)_6]^{3+}$. [86]

‡ The oxidation-reduction properties of these ions are similar.

al.[101] and Wasgestian[105] that the photochemical activity in the direct population of the ^2Eg level is due to a thermal intersystem crossing to the $^4T_{2g}$ level is correct. If the above conclusion is valid, then the total absence of the photochemical aquation of $[Cr(NH_3)_5(NCS)]^{2+}$ on excitation by sensitiser whose triplet levels lie below the $^4T_{2g}$ level but above the ^2Eg, which was discussed above, can probably be accounted for by the low probability of energy transfer from the sensitisers to the chromium(III) ions and not solely by the height of their levels.

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The data described above make it certain that the main cause of the quenching of the fluorescence of organic molecules in solutions by transition metal ions is the inductive-resonance mechanism of energy transfer. The important role of exchange-resonance energy transfer in the sensitisation of the phosphorescence of transition metal ions and of their photochemical reactions has also been convincingly demonstrated. It has been established that the rate constants for the exchange-resonance energy transfer from organic molecules to transition metal ions are lower than those for the energy transfer between organic molecules[2,4] but higher than the rate constants for energy transfer to lanthanide ions[1]. This result is consistent with the decrease of the overlapping of the π-electron clouds of organic molecules in the following sequence: (1) π electrons of another organic molecule > (2) d orbitals of transition metal ions > (3) strongly shielded f orbitals of lanthanide ions.

The application of the exchange-resonance energy transfer in the study of photochemical reactions made it possible to solve unambiguously the problem of the reactivities of individual energy levels of the ions for a number of rhodium(III), cobalt(III), platinum(III), and chromium-(III) complexes§. On the other hand, many problems still await solution: (1) only the first attempts have been made to elucidate the mechanism of the influence of the ligand on the exchange-resonance energy transfer; (2) the role of the solvent in such energy transfer is not clear; (3) the problem of whether several photochemical reactions can occur simultaneously via the same electronic state of the ion remains open; (4) it is not known whether a photochemical reaction involving an excited state of the complex proceeds as the result of the labilisation of the bonds in the latter or whether it proceeds via high vibrational levels of the ground state reached by internal conversion from the quartet state. The latter possibility is inconsistent with the experimental observation that deuteriation of amino-groups has no influence on the φ_{ph} for the complexes[92].

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§ The review does not deal with studies on energy transfer involving transition metal complexes whose lowest excited states are singlet and triplet charge transfer states[106–110]. We believe that energy transfer between such complexes and transition metal ions is analogous to the energy transfer between organic molecules and transition metal ions.

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