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Investigation of the Formation of Complexes of Organic Molecules and Lanthanide Ions in Solutions by the Electronic Energy Transfer Method

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Studies on the non-radiative energy transfer between organic molecules and lanthanide ions in solutions and on the utilisation of this phenomenon in the investigation of coordination-chemical processes involving lanthanide ions are reviewed. The bibliography includes 98 references.

CONTENTS

I. Introduction 896
II. The inductive-resonance energy transfer between organic molecules and lanthanide ions in solution 896
III. The exchange-resonance energy transfer 903

I. INTRODUCTION

We considered previously[1] the non-radiative energy transfer between organic molecules and transition metal (TM) ions and its application in the study of the mechanisms of photochemical reactions of coordination compounds. The description of the experimental data in the review was preceded by a brief account of modern ideas about the mechanisms and kinetics of non-radiative energy transfer processes†.

This review is devoted to studies of energy transfer between organic molecules and lanthanide ions in solutions. The mechanisms of energy transfer involving transition metal and lanthanide (Ln^{3+}) ions have much in common, but there are also differences. One of these is due to the fact that the chromium(III) and cobalt(III) coordination compounds, which have been most thoroughly investigated from the standpoint of energy transfer and photochemistry, exchange ligands with the surrounding medium very slowly[2]. In the case of lanthanide ions, the exchange with the solvent is fairly rapid, so that the luminescence processes and the processes involving energy transfer from and to lanthanide ions show behaviour averaged over the lifetime of their excited state. Another difference is the relatively low sensitivity of the positions and intensities of the bands in the absorption and luminescence spectra of lanthanide ions to changes in the environment compared with transition metal ions. The latter factor facilitates the study of the mechanisms of energy transfer involving lanthanide ions. For this and other reasons, the mechanism of energy transfer with participation of lanthanide ions has now been elucidated more effectively than the mechanism of the same processes involving transition metal ions. All these factors made it possible to use the energy transfer phenomenon to study complex formation reactions between lanthanide ions and organic molecules in the ground and excited states. The application of these methods has already made it possible to observe a number of new phenomena, for example the formation of hitherto unknown types of ion pairs by lanthanide ions and anionic dyes and of stable complexes between aromatic ketones and lanthanide ions, permitted an estimate of the rate of insertion of a ketone in the solvation shell of an excited lanthanide ion, etc. The prospects resulting from the application of the energy transfer method in the study of coordination-chemical processes are discussed below. These methods will probably find wide-scale applications in chemical research by virtue of their simplicity and wide scope.

† The fundamental definitions and the significance of the quantities used in the present review were also given in the previous article[1].

II. INDUCTIVE-RESONANCE ENERGY TRANSFER BETWEEN ORGANIC MOLECULES AND LANTHANIDE IONS IN SOLUTION

1. Energy and Electron Transfer from Organic Molecules in the Fluorescent State to Lanthanide Ions

For a long time, it was widely believed[3-5], on the basis of several experiments which yielded negative results, that the fluorescence of organic compounds is not quenched by lanthanide ions. Thus Rollefson and Stoughton[6] in 1941 did not observe significant quenching of the fluorescence of quinine sulphate, fluoresce in (cation), anthracenesulphonic acid, and acridonesulphonic acid by La^{3+}, Er^{3+}, Sm^{3+}, Pr^{3+}, and Nd^{3+} ions in water. Later Weiss[7,8] and Linshitz and Pekkarinen[9] were likewise unable to observe such quenching for several organic compounds.

Ermolaev and Shakhverdov[10] observed that the fluorescence of a number of dyes and aromatic hydrocarbons in solutions is strongly quenched by lanthanide ions when their fluorescence spectra overlap the most intense absorption bands of the ions. The narrowness of the absorption bands of the lanthanide ions made it possible to avoid the filtering and reabsorption effects in the quenching of the fluorescence. The dependence of the extent of quenching of the fluorescence q_0/q and of the decrease of the fluorescence lifetime (τ_{fl}) on the lanthanide concentration was found to be linear. The proportionality of the quenching rate constant to the overlap integral of the spectra ($\int_0$) shows that the fundamental quenching mechanism involves the inductive-resonance dipole–dipole (*dd*) energy transfer (Table 1) via reaction 1‡. The energy level diagram for the above type of transfer, i.e.

$$^1D^* + Ln^{3+} \rightarrow {}^1D + (Ln^{3+})^*, \qquad (1)$$

‡ Here and henceforth D, A, Ln^{3+} on the one hand and D*, A*, and $(Ln^{3+})^*$ on the other denote the energy donor molecule, the energy acceptor molecule, and the lanthanide ion in the ground and lowest excited states respectively.

is illustrated in Fig. 1. The hypothesis of energy transfer in such systems was confirmed by the observation of the luminescence of Nd^{3+} in the 8 : 1 $POCl_3$–$SnCl_4$ system sensitised by organic compounds (rubrene, trypaflavine, Acridine Orange, Acridine Yellow, etc.). The experiments on the flash photoexcitation of the systems also showed that the quenching of the fluorescence of organic compounds is not associated with their induced transition to a triplet state in the presence of paramagnetic heavy metal ions[10].

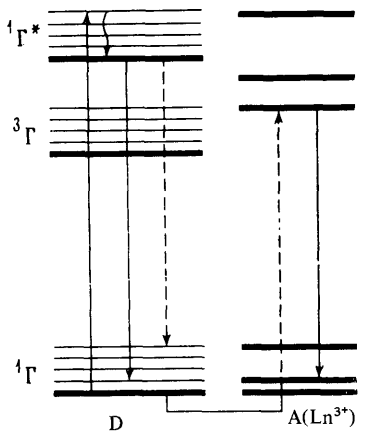


Figure 1. Schematic representation of the electronic levels in the energy transfer from organic molecules in the fluorescent state ($^1\Gamma^*$) to lanthanide ions.

The quenching of fluorescence by the Eu^{3+} ion, for which the $k_q/\int_0$ ratio is anomalously high (Table 1), involves reversible electron phototransfer via the mechanism

$$^1D^* + Eu^{3+}(^7F_0) \rightarrow {}^2D^+ + Eu^{2+}, \qquad (2)$$

as shown by Shakhverdov[11]. The Eu^{3+} ion exhibits the highest electron affinity among all the tervalent lanthanide ions[12] and can be readily reduced to Eu^{2+}. The constant k_q depends mainly on the ionisation potential of the organic molecules in the excited singlet state $I_p - E_{exc}$ (Table 2). In the flash photoexcitation of aromatic hydrocarbons in various solvents (acetone, methanol, etc.) in the presence of Eu^{3+}, a short-lived absorption due to their radical-cation ($^2D^+$) was observed; this decayed according to second-order kinetics[11]. The temperature variation of the quenching of the fluorescence of organic compounds by Nd^{3+} and Eu^{3+} ions also indicates different mechanisms of quenching by these ions.

Eisinger and Lamola[13,14] likewise found that the fluorescence of a number of biologically important compounds (for example tryptophan) is quenched by Eu^{3+} ions in H_2O and D_2O. They attributed this to energy transfer via molecular collisions, since the constant $k_q = 5 \times 10^9$ litre × mole^{-1}s^{-1} for tryptophan proved to be close to the rate constant for the reaction controlled by diffusion ($k_d \simeq 7 \times 10^9$ litre mole^{-1} s^{-1}). On this basis, they suggested[15] that Eu^{3+} be used to determine the decay times of the fluorescence of other compounds (nucleotides), assuming that $k_q = k_d$ in this case too. However, the absence of the sensitised luminescence of Eu^{3+} in the quenching of the fluorescence of tryptophan provides no grounds for such conclusion. The quenching of the fluorescence of tryptophan by the Eu^{3+} ion is probably due to reversible electron phototransfer via mechanism (2). Recent experiments by Ricci and Kilishowski[16] on the quenching of the fluorescence of indole derivatives by lanthanide ions confirm this view. They found that the Eu^{3+}, Yb^{3+}, and Sm^{3+} ions, i.e. those showing the greatest tendency towards reduction to the bivalent state, exhibit the strongest quenching effect, the rate constants for quenching by Yb^{3+} and Sm^{3+} ions being appreciably lower than the rate constant for diffusion through the solvent.

Table 1. The quenching of the fluorescence of organic compounds by lanthanide ions in acetone (293 K, in air)[10].

Donor	Acceptor	$10^{-9}k_q^*$, litre mole^{-1} s^{-1}	$10^{18}\cdot\int_0^{**}$	$10^{-26}\cdot k_q/\int_0$
Acridine Yellow	Nd^{3+}	11	7.4	14.9
	Er^{3+}	4.2	5.3	7.9
	Pr^{3+}	1.8	1.8	10.0
	Sm^{3+}	<0.1	0.9	—
	Eu^{3+}, Gd^{3+}, Ce^{3+}	<0.1	0.0	—
Perylene	Eu^{3+}	6.4	0.02	3200
	Ho^{3+}	4.3	9.6	4.5
	Pr^{3+}	2.2	6.6	3.3
	Nd^{3+}	1.7	1.6	10.6
	Ce^{3+}	0.1	0.0	—
Anthracene	Eu^{3+}	7.7	0.52	148
	Er^{3+}	1.5	1.6	9.4
	Pr^{3+}	1.0	1.1	9.1
	Dy^{3+}	0.5	0.6	8.3
	Sm^{3+}	0.4	0.6	6.7
	Nd^{3+}	~0.1	0.3	—
	Ce^{3+}	<0.1	0.0	—

*k_q is the rate constant for the quenching of the fluorescence of organic compounds by lanthanide ions.

** $\int_0 = \int_0^\infty I_D^H(\nu)\epsilon_A(\nu)\nu^{-4}d\nu$ is the overlap integral of the spectra; $I_D^H(\nu)$ is the distribution of the quantised spectral density, normalised with respect to a unit area, in the fluorescence spectrum of the energy donor and $\epsilon_A(\nu)$ is the decadic molar extinction coefficient of the energy acceptor. The values of $\ln 10 \int_0$ were adopted as the "overlap integrals" in the study of Ermolaev and Shakhverdov[10].

Table 2. The quenching of the fluorescence of organic compounds by Eu^{3+} (acetone, 293 K, in air)[11].

Electron donor	$I_p - E_{exc}$, eV	k_q, litre mole^{-1} s^{-1}	Electron donor	$I_p - E_{exc}$, eV	k_q, litre mole^{-1} s^{-1}
Anthracene	4.05	$7.7\cdot10^9$	Phenanthrene	4.51	$\sim 7.0\cdot10^8$
Perylene	4.18	$6.4\cdot10^9$	Rhodamine 6G	4.94	$7.5\cdot10^7$
Pyrene	4.21	$\sim 2.4\cdot10^9$	Trypaflavine	5.03	$\sim 10^7$
1,2-Benzanthracene	4.23	$\sim 1.6\cdot10^9$	Pyronine G	5.31	
Tetracene	4.37	$\sim 1.8\cdot10^9$	Phenosafranine	5.54	

Calculation of the critical energy transfer radius for the cases presented in Table 1 yields $R_0^{theor} \leqslant 10$ Å§. The mean square diffusion distance during the lifetime of

§The values of R_0^{theor} quoted previously[10] are somewhat too high.

the excited state ($\sqrt{\overline{r^2}}$), amounting to 40–70 Å, exceeds $3R_0^{theor}$, which leads to a linear variation of q_0/q with the acceptor concentration C_A. In order to compare the experimental results with the theory of the dipole–dipole energy transfer in liquid solutions, a study was made[17] of the quenching of the fluorescence of various dyes by Nd^{3+} ions. Table 3 presents some of the systems investigated. The distances of closest approach between the interacting molecules (R_{min}) were calculated by the summation of their radii, obtained from their molar volumes (V_M) assuming spherical symmetry. The diffusion rates were also calculated from the V_M by the familiar empirical formula of Wielke and Change[18]. The values of k_t^{theor} were obtained with the aid of a computer from these values of the parameters on the basis of the theory of dipole–dipole energy transfer developed by Rozman and coworkers for liquid solutions[19]. It is noteworthy that very similar values of k_t^{theor} were also obtained by calculations based on the Galanin-Frank[20] and Tunitskii-Bagdasar'yan[21] theories corresponding to the case of "total mixing" or "infinite" diffusion coefficients.

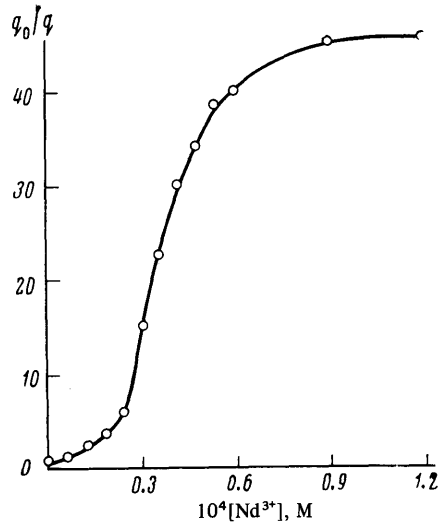


Figure 2. Dependence of the quenching of the eosin fluorescence ($C = 3.0 \times 10^{-5}$ M) on the Nd^{3+} concentration in dimethyl sulphoxide at 293 K under conditions corresponding to the formation of solvated ion pairs.

This is due to the low viscosity of acetone and the low value of R^{theor}. Table 3 shows that the experimental values of k_q for dyes exceed somewhat the values calculated theoretically. For rubrene, k_q and k_t^{theor} are virtually identical. Possibly the energy transfer for dyes with active groups is influenced by the chemical electron donor–electron acceptor interactions. The occurrence of such interactions promotes a more effective penetration of energy donors into the solvation shell of Nd^{3+}, i.e. decreases R_{min}. The fluorescence of other aromatic hydrocarbons (phenanthrene, anthracene, 1,4-benzanthracene, and pyrene) is quenched by Nd^{3+} much less effectively ($k_q > 6 \times 10^8$ litre mole^{-1}s^{-1}) owing to the low value of its overlap integral ($\int_0 < 0.06 \times 10^{17}$) with the absorption spectrum of this ion.

Table 3. The quenching of the fluorescence of organic compounds by $Nd(NO_3)_3.6H_2O$ in acetone (293 K, in air; $k_d = 2.1 \times 10^{10}$ litre mole^{-1}s^{-1})[17].

Donor	$10^9\tau_0^{fl*}$, s	$10^{-10}k_q$, litre mole^{-1} s^{-1}	$10^{17}\cdot\int_0$	q_0^{fl}	R_0^{theor}, Å	$10^{-10}k_t^{theor**}$ litre mole^{-1} s^{-1}	k_q/k_t^{theor}
Magdala Red	4.8	1.6	4.25	0.77	13.3	0.42	3.8
Quinoline Red	6.4	1.6	4.05	0.76	13.2	0.33	4.8
Rhoduline Bright Red B	2.9	1.6	3.71	0.57	12.4	0.47	3.6
Isoquinoline Red	6.3	1.4	3.86	0.87	13.4	0.36	3.9
Rhoduline Red	3.0	1.4	3.11	0.63	12.2	0.45	3.1
Phenosafranine	3.2	1.4	2.98	0.37	11.1	0.27	5.2
Safranine T	3.4	1.1	3.01	0.24	10.4	0.16	6.9
Rubrene	7.4	0.14	2.80	0.71	12.3	0.15	0.9

*The measurements of τ_0 for the fluorescence of these compounds were kindly carried out by V. Veselova on a GOI phase fluorimeter.
**The theoretically calculated rate constants for the energy transfer.

In moist acetone, where the first studies on the quenching of the fluorescence by lanthanide ions were performed, the lanthanide ions exist in the form of the neutral complexes $Ln^{3+}(NO_3^-)_3.4(5)H_2O$.[22] On the other hand, Shakhverdov showed recently[23] that, when the energy transfer takes place in water, dimethylformamide, dimethyl sulphoxide, and other solvents which are powerful electron donors (in which lanthanide ions exist in the form of triply charged complexes with neutral solvent molecules and the dyes are also employed in the form of charged ions), then such transfer is influenced significantly by the electrostatic repulsive or attractive forces between the energy donor and acceptor.

2. Energy Transfer as an Indicator of a New Type of Ion Pair (Dye–Lanthanide Ion)

In a study of the influence of the solvent on energy transfer from anionic dyes [eosin(2-)] to lanthanide ions, Shakhverdov[23] found that in such a system one can observe several types of interaction between the energy donor and acceptor. Each of these types is clearly manifested in the characteristic dependence of the fluorescence quenching on the concentration of lanthanide ions and in the absorption spectra of the dyes. The measurements made it possible to discover three cases: (1) The quenching of the fluorescence of the donor varies non-linearly with the concentration of lanthanide ions, the absorption spectrum of the dye remaining unchanged. (2) The quenching of the fluorescence increases rapidly at lanthanide concentrations comparable to the concentration of the dye, after which it reaches saturation and remains constant (in the range of C_A from 10^{-4} to 10^{-2} M and above with $C_D \simeq 10^{-5}$ M; see Fig. 2). At the same time there is some enhancement of

the absorption (by a factor up to 1.2) or a slight bathochromic shift (< 10 nm) of the absorption band. (3) The donor fluorescence is completely quenched even by low concentrations of the acceptor of the order of $C_A \simeq C_D$ and appreciable changes are observed in the absorption spectrum of the dye.

It was found that two fundamental characteristics of the solvent, namely the dielectric constant ϵ and the donor number *DN* as defined by Gutman[24], are of decisive importance for the type interaction between the dye and the lanthanide ion. The first type includes solvents with high values of ϵ or *DN*, for example formamide and water, and the second includes solvents with moderate values of ϵ and fairly high values of *DN* (glycerol, ethylene glycol, methyl and ethyl alcohols, pyridine, dimethylformamide, and dimethyl sulphoxide). The third class of solvent includes moist acetonitrile and acetone (low values of *DN* and moderate values of ϵ).

Since the energy donor and acceptor have charges of opposite signs (2- and 3+), they can remain free (I) or can form various types of solvent-separated (II) or contact (III) ion pairs as well as covalent complexes (IV):

$$\underset{(I)}{D^{2-} + A^{3+}} \rightleftharpoons \underset{(II)}{D^{2-}|\text{solvent}|A^{3+}} \rightleftharpoons \underset{(III)}{D^{2-}, A^{3+}} \rightleftharpoons \underset{(IV)}{D^{2-}:A^{3+}}. \quad (3)$$

It was natural to relate the observed behaviour of the system to the above scheme. Indeed, for high values of ϵ and *DN*, the attraction between ions with different charges is reduced; this does not favour their aggregation. On the other hand, an appreciable decrease of these parameters can lead to the formation of a complex of the dye and the lanthanide ions. It has been suggested[23] that the permanent quenching of the fluorescence of dyes by lanthanide ions in solvents of the second type is due to the energy transfer from $^1\Gamma^*$ states of the dye to the acceptor within ion pairs. This hypothesis is confirmed by the observation of the eosin-sensitised luminescence of Nd^{3+} in dimethylformamide and d_6- and h_6- dimethyl sulphoxide. The correlation between k_q and $\int_O$ for four ions absorbing in the region of the fluorescence of D ions (Table 4) permits the conclusion that the mechanism of energy transfer in the postulated ion pairs is of the dipole–dipole (*dd*) type. The slightly higher value of $k_q/\int_O$ for Nd^{3+} compared with other ions may be due to the contribution to its $\int_O$ via the $^4I_{9/2} \rightarrow {}^4G_{5/2;7/2}$ transitions, which are allowed, being of the quadrupole type.

The observed quenching of fluorescence by non-absorbing ions may be explained by electron phototransfer within ion pairs. It is known[12,25] that Eu^{3+}, Sm^{3+}, and Yb^{3+} ions are capable of reversible photochemical reduction to the bivalent state and Ce^{3+}, Dy^{3+}, and Tb^{3+} ions are capable of reversible photochemical oxidation. Electron phototransfer processes with participation of free Eu^{3+} and Ce^{3+} ions have been investigated by Shakhverdov[11]. When an excess of $Gd(NO_3)_3$ is added to a solution of eosin in dimethylformamide, the fluorescence of which has been quenched by $Nd(NO_3)_3$, the eosin fluorescence is re-established and can be restored almost to the initial level. The effect of $Gd(NO_3)_3$ can be explained by the displacement of Nd^{3+} as the counterion from the [eosin(2-) ... Nd^{3+}] ion pair and its replacement by Gd^{3+}, which hardly quenches the fluorescence of the dye. The composition of the ionic associated species has been determined by spectrophotometrical analytical methods[26] [the isomolar series (continuous variations) and molar ratios methods] in dimethyl sulphoxide at 293 K (it was indeed found to be 1 : 1) together with its instability constant, which proved to be 9.4×10^{-7} mole litre^{-1}.

Assuming a *dd* energy transfer mechanism for the quenching of the fluorescence of eosin in ion pairs with Nd^{3+}, Ho^{3+}, Pr^{3+}, and Er^{3+}, the distances between the ions in such pairs were calculated by the Förster–Galanin theory[23,26]. Values ranging from 6.2 to 7.3 Å were obtained (Table 4), i.e. approximately equal to the sum of the radii of the dye and the solvated lanthanide ion. We obtained similar values of *R* (R_{min}) in a study of the reverse energy transfer from Tb^{3+} to eosin in water, where the ions are not bound in pairs[27]. Thus the distance between the components of the ion pair can be determined by studying the energy transfer, which is of considerable interest.

Table 4. The quenching of the fluorescence of eosin (2-) in ion pairs with lanthanide ions in dimethylformamide (293 K; $C_{eosin} \simeq 5 \times 10^{-6}$ M; $\tau_0^{fl} = 3.9 \times 10^{-9}$ s; $q_0^{fl} = 0.76$)[23].

Quenching agent	q_0/q	k_q, s^{-1}	$10^{18} \int_0$	$10^{-26} k_q \int_0$	*R*, Å
Nd^{3+}	49	$1.23 \cdot 10^{10}$	26.4	4.7	6.2
Ho^{3+}	4.0	$7.7 \cdot 10^8$	4.26	1.8	7.3
Pr^{3+}	3.8	$7.2 \cdot 10^8$	3.06	2.3	7.0
Er^{3+}	3.1	$5.4 \cdot 10^8$	1.99	2.7	6.8
Gd^{3+}	1.1	$2.1 \cdot 10^7$	0.00	—	—
La^{3+}	1.0	$<10^7$	0.00	—	—
Eu^{3+}	9.7	$2.2 \cdot 10^9$	<0.01	>2200	—
Sm^{3+}	2.6	$4.1 \cdot 10^8$	0.00	—	—
Yb^{3+}	1.2	$5.1 \cdot 10^7$	0.00	—	—
Ce^{3+}	2.4	$3.6 \cdot 10^8$	0.00	—	—
Dy^{3+}	2.4	$3.6 \cdot 10^7$	0.00	—	—
Tb^{3+}	1.7	$1.8 \cdot 10^8$	0.00	—	—

*The first-order rate constants determined from the change in the intensity of the fluorescence of eosin in the presence of lanthanide ions.

We are not aware of data obtained by other methods concerning the possible existence of ion pairs comprising dyes and lanthanide ions¶. The concept of ion pairs is widely used nowadays in the investigation of the interaction of radical-anions and organic carbanions with alkali metal ions[29].

It is noteworthy that the relative extents of quenching of the fluorescence of eosin by lanthanide ions, determined from the decrease of the yield q_0/q and of $\tau_{fl} = \tau_0/\tau$, are not equal. τ was measured with the aid of a phase fluorimeter. $q_0/q = 4.0$ and $\tau_0/\tau = 1.7$ were obtained for Ho^{3+} ions. This difference may be due to both the simultaneous coexistence in solution of several types of ion pairs and to partial dissociation of the ion pairs into individual ions.

The ion pairs formed in aqueous solutions are highly dissociated. The quenching of the fluorescence of eosin by lanthanide ions is in this case slight, is manifested at much higher concentrations than in dimethylformamide and dimethyl sulphoxide ($q_0/q \simeq 4$ for $C_{Nd^{3+}} = 0.04$ M), and is not accompanied by a decrease of τ_0^{fl}. The p*K* values

¶The presence of ion pairs of another type involving cationic dyes and lanthanide ions, where the interaction takes place via the anions (Cl^-, Br^-) associated with the dye, has been suggested[28] in a study of the NMR shift induced by lanthanides.

for the 1 : 1 eosin–Nd^{3+} ion pairs in water, measured by the equilibrium shift method modified to allow for quenching of luminescence, were found to be 1.64, 1.79, 1.96, 2.13, and 2.32 at pH 5.5 and ionic strengths of 0.48, 0.24, 0.12, 0.06, and 0.03 respectively. Extrapolation to zero ionic strength (using the Davies equation[30]) yields $pK = 2.85$, i.e. $K = 1.4 \times 10^{-3}$ M. It is noteworthy that the spectrophotometric methods do not yield in this case any information, since the formation of eosin–Nd^{3+} ion pairs ($C \leqslant 0.04$ M) is not accompanied by a change in the absorption spectra. The neutralisation of lanthanide ions in aqueous solutions containing eosin following the addition of sodium acetate, sodium sulphate, sodium nitrate, etc. leads to an appreciable decrease in the efficiency of the fluorescence quenching[22]. The anions of the above salts are more likely to form complexes with Ln^{3+} than in eosin. The sequence of the inhibiting effects of the anions is satisfactorily correlated with the stability constants of their complexes with lanthanide ions.

Table 5. Comparison of the calculated (R_0^{theor}) and experimental (R_0^{exp}) critical radii for energy transfer from $Eu(TTA)_3Phen$ to dyes {2 : 1 ethanol–ether; 77 K; $[Eu^{3+}] \simeq 10^{-4}$ M; $\tau_0^{lum} \simeq 0.7$ ms}[31,32].

Acceptor	R_0^{exp}, A	R_0^{theor}, A
Aniline Blue	70	72
Brilliant Green	70	72
Cyan Blue	71	71
Turquoise Blue G**	70	70
Victoria Blue 4R	56	67
Victoria Blue R	57	66
Methyl Violet	51	57

*TTA = thenoyltrifluoroacetonate and Phen = 1,10-phenanthroline.

**The above dye (Türkis blau G) has been incorrectly referred to in some studies[31-33] as "Turkish Blue G".

***The values of R_0^{theor} were calculated on the assumption that $\bar{\Phi} = \sqrt{2}/3$. According to Maksimov and Rozman[37], $\bar{\Phi} = 0.845\sqrt{2}/3$ for solid solutions, but we were unable to correct R_0^{theor} because q_{OD} was somewhat too high.

3. Energy Transfer from Lanthanide Ions to Dyes in Solutions

Ermolaev and Shakhverdov[31-33] investigated the non-radiative energy transfer from excited lanthanide ions (Eu^{3+}, Tb^{3+}) to dyes in solid and liquid solutions when the luminescence spectra of Eu^{3+} and Tb^{3+} overlapped the intense absorption bands of the dyes. The lanthanide ions were used in the form of complexes with organic ligands and also as their nitrate salts. It was shown that the addition of dyes (anionic and cationic) to the solid solutions containing Eu^{3+} leads to a decrease of the yield and a shortening of τ—the luminescence time of the ion. The quenching was accompanied by the appearance of the sensitised fluorescence of the dyes. By comparing the concentrations of the acceptor which correspond to the quenching of the fluorescence by a factor of two and the $\int_O$ for the spectra, it was shown[31] that the quenching is due to the inductive-resonance dipole–dipole energy transfer. In conformity with the Förster–Galanin theory, the relative decrease of τ was smaller than the relative decrease of the luminescence yield. At the same time, deviations of the rate of decay of the luminescence from the exponential relation were observed for the quenched solid solutions. The calculated dependence of the efficiency of the quenching of the Eu^{3+} luminescence on the concentration of acceptors and the luminescence decay law for dipole–dipole energy transfer in Refs. 34–36 agreed satisfactorily with experimental data. Table 5 presents several values of the theoretical critical energy transfer radii and compares them with the R_0^{exp}. Evidently the agreement for the first four pairs is satisfactory; the poorer agreement for the last three combinations we believed to be caused by the greater tendency of these dyes towards dimerisation under the experimental conditions.

Thus one can claim with confidence that the quenching of the luminescence of lanthanide ions by dyes in solid solutions is due to *dd* energy transfer when there is no chemical interaction between them leading to a change in the absorption spectra:

$$^1(Ln^{3+})^* + {}^1A \rightarrow Ln^{3+} + {}^1A^* , \qquad (10)$$

where ^1A and $^1A^*$ are the molecules of the energy acceptor (dye) in the ground and excited singlet states. The energy level diagram for energy transfer of this type is illustrated in Fig. 3.

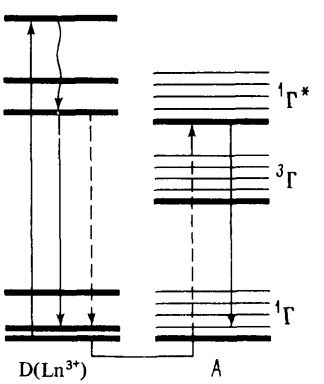


Figure 3. Schematic illustration of the electronic levels in the energy transfer from lanthanide ions to organic dyes with excitation of the singlet excited levels of the latter.

In order to investigate the influence of diffusion on the above energy transfer a study was made of the quenching of the luminescence of Tb^{3+} compounds in liquid solutions[32,33]. The values of $\int_O$ were varied widely (within the limits of three orders of magnitude); compounds with $\int_O = 0$ were also used. It was noted that τ_0^{lum} decreased, but, in contrast to the solid solutions, the quenching of the Tb^{3+} luminescence remained exponential. The absolute quenching rate constants k_q were obtained from the Stern–Volmer relations between τ_0^{lum}/τ^{lum} and C_A. It was found that the values of $k_q/\int_O$ remained approximately the same, which provided evidence for the assumption that in liquid solutions the quenching of the luminescence of lanthanide ions is caused also by *dd* energy transfer. For

low values of $\int_O$ and $\int_O = 0$, exchange interactions leading to the excitation of the triplet states of the organic molecules† contributed to the quenching of the luminescence. However, the rate constants for such processes were low ($\leq 3 \times 10^5$ litre mole^{-1}s^{-1}) compared with energy transfer to the singlet states.

Table 6 presents data obtained by Shakhverdov and Ermolaev[33] for the quenching of the $Tb(Sal)_3$ luminescence by a number of dyes‡. The measured k_q were compared with the values calculated from the theory of *dd* energy transfer in the presence of diffusion[19] and reasonably satisfactory agreement between them was obtained, bearing in mind the uncertainty in the parameter R_{min}. Table 6 also lists the values of R_{min}^{theor} calculated for the condition that $k_q = k_t^{theor}$. The discrepancy between k_q and k_t^{theor} for $Tb(NO_3)_3$ is greater than for $Tb(Sal)_3$:[33] in the latter case, additional electron donor–electron acceptor interactions between Tb^{3+} and the dyes probably contribute to the energy transfer. Analysis of the results showed that energy transfer from lanthanide ions can be described satisfactorily in terms of the conclusions derived from theories based on the case of infinite diffusion coefficients (Galanin[38], Galanin-Frank[20], Tunitskii–Bagdasar'yan[21]). The mean square diffusional distance ($\sqrt{\bar{r}^2}$) during the period τ_{OD} is approximately 2×10^4 Å, which greatly exceeds R_0^{theor}. This is responsible for the exponential decay of the luminescence of the quenched solutions and for the linearity of the relation $\tau_0/\tau = q_0/q = f(C_A)$. By altering the temperature, it is possible to vary $\sqrt{\bar{r}^2}$. Thus energy transfer from lanthanide ions to dyes constitutes a convenient model for the investigation of the influence of diffusion and dipole–dipole energy transfer.

Table 6. The quenching of the luminescence of $Tb(Sal)_3^*$ by dyes {methanol; 293 K; $[Tb^{3+}] = 2 \times 10^{-4}$ M; $\tau_0^{lum} = 1.0 \times 10^{-3}$ s}[33].

Acceptor	$10^{-6}k_q$, litre mole^{-1} s^{-1}	$10^{14} \cdot \int_0$	$10^{-20} \cdot k_q / \int_0$	R_0, Å	R_{min}, Å	$10^{-6}k_t^{theor}$, litre mole^{-1} s^{-1}	$\frac{k_q}{k_t^{theor}}$	k_{min}^{theor}, Å
Fuchsine	309	57.6	5.4	60.9	9.7	139	2.2	7.5
New Fuchsine	216	40.6	5.3	57.5	9.9	92.8	2.3	7.5
Safranine T	117	19.4	5.9	51.0	9.7	48.2	2.4	7.3
Magdala Red	83.4	15.6	5.4	49.0	10.1	33.5	2.5	7.6
Acridine Orange	12.9	2.20	5.9	35.3	9.5	5.62	2.3	7.3
Coryphosphine	10.7	1.34	8.0	32.6	9.4	3.62	2.9	6.6
Chrysoidine	9.7	1.14	8.5	31.9	9.2	3.37	2.9	6.5

*Sal = salicylate anion (Ed. of Translation).

The change in the overall diffusion coefficients from 10^{-5} cm^2 s^{-1} to infinity for the overall energy transfer from lanthanide ions to dyes ($R_0^{theor} \simeq 60$ Å) has no effect whatever on the transfer rate constant. This greatly facilitates the study of the influence of the chemical nature of the solvent on the energy transfer. Our data for energy transfer from $Tb(NO_3)_3$ to fuchsin are presented in Table 7. In order to compare experiment with theory, the values of R_0^{theor} were calculated in all cases from the $\int_O$ and q_{OD}^{fl}. We obtained the theoretical values of k_t^{theor} from the Tunitskii–Bagdasar'yan formula[21] [see also Eqn. (6) in Ref. 1], assuming that $R_{min} = 8$ Å. The influence of Coulombic interaction on the energy transfer between fuchsin and Tb^{3+} ions, which are positively charged (the 1+ ... 3+ system), is in this case small (see subsection 4) and was disregarded.

Table 7. The quenching of the luminescence of $Tb(NO_3)_3$ by fuchsine in various solvents {$[Tb^{3+}] = 0.02$ M; 293 K}.

Solvent	ϵ	*DN*	$10^{-8}k_q$, litre mole^{-1} s^{-1}	R_0, Å	$10^{-8}k_t^{theor}$, litre mole^{-1} s^{-1}	$\frac{k_q}{k_t^{theor}}$	R_{min}^{theor}, Å
Acetonitrile	38.0	14.1	7.4	51.9	1.0	7.4	4.1
Acetone	20.7	17.0	7.0	54.3	1.3	5.4	4.5
Pyrdine	12.3	33.1*	2.8	46.0	0.52	5.4	4.6
Methanol	31.2	—	4.5	53.1	0.91	4.9	4.8
Water (H_2O)	81.0	18.0	0.86	37.0	0.28	3.1	5.5
Water (96% D_2O)	79.0	—	0.61	46.9	0.23	2.7	5.8
Tributyl phosphate	6.8	23.7	1.4	55.0	0.61	2.3	6.1
Dimethylformamide	36.1	26.6	1.8	56.1	0.95	1.9	6.5
Dimethylsulphoxide	45.0	29.8	0.72	51.7	0.47	1.5	7.0

*The values of *DN* for the solvents were determined by Gutmann[24] relative to $SbCl_5$. For lanthanide ions, coordination via the nitrogen atom is weaker than via the oxygen atom. Thus the value *DN* quoted for pyridine is much too high in relation to other solvents as regards interaction with lanthanide ions.

Comparison of the theory and experiment showed that the efficiency of such transfer (i.e. k_q/k_t^{theor}) decreases with enhancement of the electron-donating properties of the solvent (*DN*) and is independent of ϵ (see Table 7). The deviation of pyridine from the above series, observed by Ermolaev and coworkers[39,40], is due to the specific features of its interaction with lanthanide ions. The decrease of the ratio k_q/k_t^{theor} with increase of *DN* may be accounted for by the increase of R_{min}. It is known that an increase of *DN* for solvents entails an increase in their solvating capacity in relation to lanthanide ions. This leads to an increase of the size of the first coordination sphere of such ions. Furthermore, in solvents which are powerful electron donors there is also a possibility of a certain degree of order also in the second coordination sphere of the lanthanide ions, which prevents its penetration by dyes. In solvents which are weak electron donors (acetone, acetonitrile), dyes are also apparently capable of becoming incorporated in the first coordination sphere. Indeed, theoretical calculation of R_{min}^{theor} for solvents of this type (on the basis of the condition $k_q = k_t^{theor}$) yields very low values (down to 4.1 Å). Some influence of the *DN* for solvents on the reverse transfer (from dyes to lanthanide ions) has also been noted, but in this case it is masked by the influence of solvent viscosity.

†See Section III below.

‡Sal = salicylate anion.

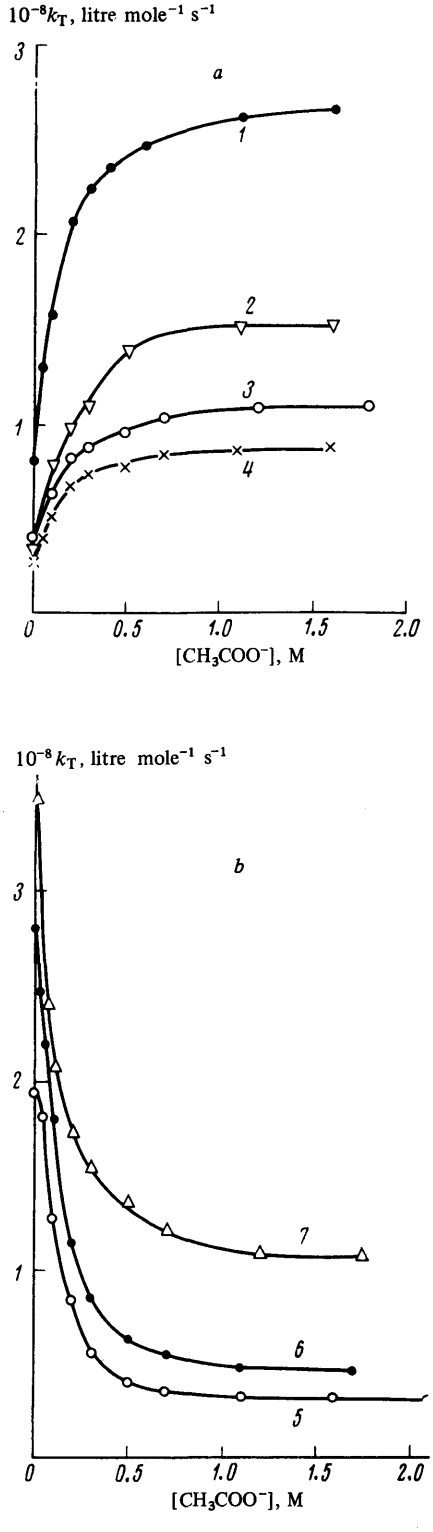


Figure 4. Dependence of the rate constant for the quenching of the Tb^{3+} luminescence (C = 0.03 M) by various dyes in water on the CH_3COONa concentration: *a*) the (3+...1+) system [quenching agent: 1) fuchsine; 2) phenosafranine; 3) new fuchsine; 4) safranine T]; *b*) the (3+...2-) system [quenching agent: 5) acid fuchsine; 6) eosin; 7) erythrosin].

4. The Influence of Electrostatic Interactions of the Donor and Acceptor on the Efficiency of Energy Transfer

We have considered hitherto non-radiative energy transfer mainly between neutral complexes of lanthanide ions and dyes. However, in many solvents lanthanide ions and dyes exist in the form of charged ions. In this case, the rate of non-radiative energy transfer is influenced also by the forces of the electrostatic interaction between the donor and acceptor. Shakhverdov and Bodunov[23,32,41] demonstrated such influence in the energy transfer from the free Tb^{3+} ion in water to anionic (2-) and cationic (1+) dyes, the results being compiled in Table 8, which shows that the efficiency of the quenching of the Tb^{3+} luminescence by dyes (the $k_q/\int_0$ ratio) depends markedly on the sign of the charge of the latter. The interaction of anionic dyes with lanthanide ions is much more effective. To demonstrate the electrostatic nature of the influence of the acceptor charge, sodium acetate (CH_3COONa), whose anions form neutral complexes with Tb^{3+}, was introduced into the solution. This resulted in the opposite effect on the (3+ ... 1+) and (3+ ... 2-) systems. In the former case k_q decreased and in the latter increased (Fig. 4); the values of $k_q/\int_0$ became equal under these conditions. The limiting quenching constants in the presence of sodium acetate (k_q') and $k_q'/\int_0$ are listed in Table 8.

Table 8. The quenching of the luminescence of $Tb(NO_3)_3$ by organic dyes in water {$[Tb^{3+}] = 0.03$ M; $\tau_0^{lum} = 4.5 \times 10^{-4}$ s; $\tau_0'^{lum} = 7.0 \times 10^{-4}$ s; 293 K}[41].

Acceptor	$10^{-7}k_q$, litre mole^{-1} s^{-1}	$10^{-7}k_q'$, litre mole^{-1}s^{-1}	$10^{-20}\frac{k_q}{\int_0}$	$10^{-20}\frac{k_q'}{\int_0}$	$\frac{k_q'}{k_q}$	$\frac{k_t'^{theor}}{k_t^{theor}}$ (13H$_2$O)	$\frac{k_t'^{theor}}{k_t^{theor}}$ (6H$_2$O)
(3+...1+) System							
Fuchsine	8.6	26.7	2.8	8.7	3.1	2.8	2.7
Safranine T	2.9	8.6	2.9	8.7	3.0	2.8	2.8
New Fuchsine	3.9	10.8	1.3	3.6	2.8	2.7	2.7
Phenylsafranine	3.6	15.0	2.2	10.4	4.7	2.9	2.8
Rhoduline Red B	0.71	2.3	1.1	3.7	3.2	2.7	2.7
(3+...2-) System							
Acid Fuchsine	19.5	3.2	34.8	5.7	0.16	0.47	0.26
Eosin	28.4	4.7	16.3	2.7	0.16	0.42	0.22
Erythrosin	35.5	10.5	20.1	6.0	0.29	0.45	0.23
Bengal Rose	59.7	14.0	20.0	4.7	0.23	0.45	0.24

The results of the above experiments were compared with theoretical computer calculations based on Bodunov's theory[42,43], taking into account the influence of the electrostatic interaction between the ions on the dipole–dipole energy transfer. The calculations were performed for two cases, differing in the size of the hydration shell of Tb^{3+}. In the first case, it was assumed that the entire hydration shell (known to comprise approximately 13 water molecules according to diffusion data) determines the value of R_{min}. In the second case, account was taken only of the immediate environment of Tb^{3+} (six water molecules). In the calculations, the change in R_0^{theor}, R_{min}, and τ_0^{lum} on formation of Tb^{3+} complexes with CH_3COO^- was also taken into account. This leads in all cases to an increase of $k_t'^{theor}/k_t^{theor}$ by factors of 1.8

and 1.3 respectively. There was a difference between the absolute values of k_q and k'_q determined experimentally and calculated theoretically. The reason for this is not altogether clear and, as stated above, is apparently due to the solvent. On the other hand, the effect of the electrostatic interactions on the energy transfer is described fairly satisfactorily by the theory[42,43]. Table 8 lists the experimental (k'_q/k_q) and theoretical ($k_t'^{theor}/k_t^{theor}$) ratios of the rate constants for the quenching of the Tb^{3+} luminescence by dyes with and without sodium acetate. Evidently, in the system with Coulombic repulsion between the ions (3+ ... 1+), the change in the parameter R_{min} has no influence whatever on the theoretical rate constant ratio and corresponds to the experimental values of k'_q/k_q. On the other hand, the system with a Coulombic attraction between the ions (3+ ... 2-) is more sensitive to this parameter. The agreement with experiment in this system is found to be better when account is taken of only the first coordination sphere of Tb^{3+}.

5. Energy Transfer from Lanthanide Ions to Organic Radical-Ions

It was of interest to investigate the influence of the multiplicity of the energy states of the energy acceptors on the mechanism of the energy transfer from lanthanide ions. For this purpose, Shakhverdov[44] used for acceptors the radical-cations of aromatic hydrocarbon with a doublet ($^2\Gamma$) ground state. One could then expect the occurrence of an exchange energy transfer, since the Wigner rule (overall spin conservation) holds under these conditions. The experiments were performed in sulphuric acid at 293 K. The quenching of the Tb^{3+} and Eu^{3+} luminescence by three radical-cations was investigated (Table 9). At the same time, experiments were performed with acceptors having a $^1\Gamma$ ground state (the proton complex of tetracene, etc.). In both cases, the experimental results were compared with theory (assuming that R_{min} = 8 Å). It was shown that the quenching of the luminescence of lanthanide ions by an organic radical is due to *dd* energy transfer. An estimate of the probability of electron phototransfer in such systems showed that it cannot compete with energy transfer. Indeed k_q for the quenching of the Tb^{3+} luminescence in sulphuric acid by one of the most powerful electron acceptors (Ce^{4+} ions) proved to be only $\sim 1.2 \times 10^6$ litre mole^{-1}s^{-1}. In the quenching of the Eu^{3+} luminescence by powerful organic electron donors (diphenylamine and triphenylamine) and in the quenching of the Tb^{3+} luminescence by electron acceptors (chloranil, bromanil, *p*-benzoquinone, and *sym*-trinitrobenzene), the values of k_q are likewise low. Thus $k_q \leq 2.2 \times 10^6$ litre mole^{-1}s^{-1} for the quenching of the Tb^{3+} luminescence (in methanol) and $k_q \leq 4.8 \times 10^5$ litre mole^{-1}s^{-1} for Eu^{3+} (in acetone). The change in the multiplicity of the ground state of the acceptors (from $^1\Gamma$ for dyes to $^2\Gamma$ for radicals) did not therefore lead to a change in the mechanism of the energy transfer.

III. THE EXCHANGE-RESONANCE ENERGY TRANSFER

The exchange-resonance energy transfer between the donor and the acceptor requires overlap of their electron clouds[45,46], which is also needed for the formation of a covalent bond between them. Indeed, a definite correlation can be established in many instances between energy transfer and complex formation. It is particularly pronounced for the interaction of triplet ketones with lanthanide ions and of excited lanthanide ions with aromatic ketones, leading to energy transfer from the excited triplet levels of the latter. Energy transfer involving lanthanide ions to and from the triplet level of organic molecules takes place via the exchange-resonance mechanism[47-49]. As will be shown below, this is why the study of this type of energy transfer has proved particularly fruitful in the development of methods for the investigation of complex formation in solutions.

Table 9. The quenching of the luminescence of lanthanide ions in 95% sulphuric acid at 293 K[44].

Acceptor	$10^{-7}k_q$, litre mole^{-1}s^{-1}	$10^{14}\int_0$	$10^{-20}\frac{k_q}{\int_0}$	R_0, Å	$10^{-7}k_t^{theor}$, litre mole^{-1} s^{-1}	$\frac{k_q}{k_t^{theor}}$	R_{min}^{theor}, Å
Tb^{3+} donor (C = 0.01 M, $\tau_0 = 2.4 \times 10^{-3}$ s)							
Perylene$^+$	12	25.8	4.7	54	5.0	2.4	6.0
9,10-Diphenylanthracene$^+$	3.6	6.7	5.4	13	1.3	2.8	5.8
Tetracene$^+$	0.65	1.5	4.3	33	0.29	2.2	6.1
(Tetracene)H$^+$	1.9	3.5	5.4	39	0.66	2.9	6.7
Eu^{3+} donor (C = 0.01 M, $\tau_0 = 1.2 \times 10^{-3}$ s)							
9,10-diphenylanthracene$^+$	7.2	15.6	4.6	48	4.8	1.5	7.0
Perylene$^+$	5.7	7.6	7.5	42	2.3	2.5	6.0
Tetracene$^+$	2.9	5.6	5.2	40	1.7	1.7	6.5
(Tetracene)H$^+$	3.7	7.4	5.0	42	2.3	1.6	6.8

1. Energy Transfer from the Triplet States of Organic Molecules to Lanthanide Ions

(a) Solid solutions. The first experiments on these lines were published by Smaller et al.,[50] who observed a marked decrease of the amplitude of the ESR signal of the triplet molecules of perdeuteronaphthalene in a 9 : 1 methanol–water solution at 77 K in the presence of Gd^{3+} ions. They believed that the mechanisms of this quenching involved the intercombination transition $^3\Gamma \rightsquigarrow \Gamma_0^1$ catalysed by the paramagnetic ion. Indeed the Gd^{3+} ion has a high magnetic moment (8.2 μ_B). In addition, they also observed a non-rigorous correlation between the rate of quenching of the triplet state and the magnetic moments of Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Fe^{2+}, and Gd^{3+} ions.

Breuninger and Weller[51] recently investigated the influence of the addition of Gd^{3+}, La^{3+}, and Tb^{3+} ions on the luminescence of perdeuteronaphthalene and triphenylene in a 9 : 1 methanol–water solid solution at 77 K. The fluorescence of naphthalene and triphenylene is not quenched by lanthanide ions up to a concentration of the latter of 0.5 M. The phosphorescence of both hydrocarbons is quenched by Tb^{3+} ions, but not Gd^{3+} and La^{3+} ions. They showed that the decreased amplitude of the ESR signal of triplet perdeuteronaphthalene in the presence of Gd^{3+}, observed by Smaller et al.,[50] is due exclusively to the broadening of the ESR lines of the triplet molecules and not to a decrease in their concentration.

Breuninger and Weller[51] explained the quenching of the phosphorescence of organic molecules by Tb^{3+} (and transition metal) ions as a consequence of non-radiative

energy transfer. The occurrence of energy transfer is confirmed by the observation of the triphenylene-sensitised Tb^{3+} luminescence. The energy transfer in the case of Tb^{3+} has an exchange-resonance mechanism; this is supported by the exponential variation of the quenching of the phosphorescence (q_{OD}/q_D) with the concentration of the energy acceptor (Tb^{3+}) and by the approximately tenfold difference between the slopes of the q_{OD}/q_D and τ_{OD}/τ_D curves as a function of Tb^{3+} concentration. The critical radii R_0 and ρ^{-1}§ for the transfer from perdeuteronaphthalene and triphenylene to Tb^{3+} are respectively 11.0 Å and 0.10 for perdeuteronaphthalene and 13.6 Å and 0.14 for triphenylene. The values of R_0 and the ratios of the slopes obtained for the systems investigated are close to the analogous quantities for the triplet–triplet energy transfer between organic molecules in solid solutions via the exchange-resonance mechanism[46,52,53].

The high efficiency of energy transfer from the $^3\Gamma$ states to the Tb^{3+} ion has been explained[51] by the incorporation of the energy donors in the solvation shell of the ion and the formation of complexes. We believe that this explanation is not very probable for the system investigated, since the inner coordination shell comprises polar water and alcohol molecules and their displacement by non-polar aromatic hydrocarbon molecule is unlikely.

The quenching of the benzoquinone phosphorescence by lanthanide ions in solid alcohols at 77 K was investigated by Gevorkyan[54]. An exponential relation was observed between the quenching and the concentrations of Nd^{3+}, Eu^{3+}, and Tb^{3+} ions. The critical transfer distances are 13.0 Å for Nd^{3+}, 12.0 Å for Eu^{3+}, and 11.0 Å for Tb^{3+}. The ratio ρ is close to 10 for quenching by Eu^{3+} and Tb^{3+} and of the order of 4–6 for quenching by Nd^{3+}. We suggest that in the case of Eu^{3+} and Tb^{3+} the exchange-resonance mechanism is decisive, while quenching by Nd^{3+}, which has more intense absorption bands, involves both exchange-resonance and inductive-resonance energy transfer mechanisms.

The energy transfer from two ketones (methyl 2-naphthyl ketone and 2-fluorenyl methyl ketone) to Eu^{3+} and Tb^{3+} ions in solid solutions (1 : 4 methanol–ethanol) at 77 K has been investigated by Minn et al.[55,56] They established the occurrence of energy transfer from the decrease in the decay time and in the intensity of the phosphorescence of the ketones in the presence of lanthanide ions and also from the appearance of the sensitised Eu^{3+} and Tb^{3+} luminescence. Their quantitative data are in poor agreement with modern ideas concerning any of the known mechanisms of non-radiative energy transfer in solid solution. The effective Bohr radii quoted by the authors[55,56] for the system investigated, namely $L = 4.5$–20 Å, also appear to be extremely doubtful, since $L < 2$ Å even for the triplet–triplet energy transfer between two aromatic molecules and the rate of decrease of the electron density for the $4f$ shell of the lanthanide ion must be greater than the rate of decrease of the π-electron density. The mechanism of energy transfer from aromatic ketones to lanthanide ions in solid solutions requires additional investigation.

(b) Liquid solutions. The role of complex formation. Porter and Wright[57] observed the quenching of the triplet state of naphthalene by neodymium ions in ethylene glycol at 298 K; $k_q = 4 \times 10^5$ litre mole^{-1}s^{-1}, which is lower by three orders of magnitude than the diffusion rate constant under the same conditions ($k_d = 3.7 \times 10^8$ litre mole^{-1}s^{-1}). It was suggested that the effect is due to the intercombination degradation of the triplet molecule to the ground state catalysed by the lanthanide ion:

$$^3D + {}^nLn^{3+} \rightsquigarrow {}^1D + {}^nLn^{3+}. \qquad (11)$$

Matovich and Suzuki[58] and other investigators[59–64] demonstrated the sensitisation by the solvent of the luminescence of Eu^{3+}, Sm^{3+}, Tb^{3+} and Dy^{3+} ions dissolved in aromatic ketones. The phenomenon is due to the non-radiative energy transfer from the lowest triplet levels of the ketones to lanthanide ions:

$$^3D + {}^nLn^{3+} \rightarrow {}^1D + {}^m(Ln^{3+})^*;$$
$$^m(Ln^{3+})^* \rightarrow {}^nLn^{3+} + h\nu_{s.l.} \qquad (12)$$

The fact that the intramolecular energy transfer in complexes of lanthanide ions with organic compounds observed previously[65–68] did not occur under these conditions was demonstrated by the following findings: (1) the coincidence of the absorption spectra of the ketone and the ketone–lanthanide ion system in the range 300–400 nm, where lanthanide ions do not exhibit an absorption comparable to that of ketones; (2) by the disappearance of the sensitised luminescence on freezing. The intensity of the sensitised luminescence of lanthanide ions in ketones increased with increase in the temperature of the solution. On the other hand, Faidysh and coworkers[69] observed a decrease in the intensity of the sensitised luminescence of $Eu^{3+}(NO_3^-)_3$ dissolved in benzophenone with increase of temperature and the sensitised luminescence did not disappear even at 77 K. A complication which prevented an unambiguous interpretation of these relations[58,66] is the migration of the energy of the triplet excitation via the molecules of the aromatic ketones until their capture by the lanthanide ion. Zolin and coworkers[70–72] extended the range of energy donors by sensitising the lanthanide ions with dyes and certain heteroaromatic compounds.

Ermolaev and coworkers[73–78] investigated the kinetics of the energy transfer from aromatic ketones with lowest triplet states of the n, π^* and π,π^* types to lanthanide ions in solutions. The diffusional mechanism of energy transfer and the involvement in the latter of the lowest triplet state of ketones were demonstrated by the method involving competition between the transfer to the lanthanide ion and the triplet–triplet transfer of energy to the acceptor (see Scheme 1 below).

The study of the dependence of the intensity of the benzophenone-sensitised luminescence of Eu^{3+} on its concentration and on the concentration of the triplet energy acceptor (naphthalene) showed that (1) the transfer takes place from the lowest triplet level of the ketone (see Fig. 5), (2) the rate of energy transfer is proportional to the concentration of the ion and independent of the concentration of the ketone, and (3) the quenching of the benzophenone-sensitised luminescence of the lanthanide ion (Eu^{3+}) by the triplet energy acceptor (naphthalene) obeys the Stern–Volmer relation and it follows from the slope of the linear plot that the rate constant for the energy transfer from the ketone to Eu^{3+} in acetone is almost two orders of magnitude lower than the diffusion rate constant k_d and the conclusion reached by Heller and Wasserman[62] and Filipescu and Mushrush[79] that $k_t = k_d$ for the solvent is therefore incorrect. The later conclusion that $k_t \ll k_d$ was confirmed by Wagner and Schott[80], using the same method, and by Ermolaev and Tachin[74], using the method of flash photoexcitation, from the decay of the triplet–triplet

§ $\rho = \lim_{C_A \to 0} \frac{d(q/q_0)}{dC_A} \frac{d(\tau/\tau_0)}{dC_A}$.

absorption. Table 10 lists the rate constants for the energy transfer from triplet ketones to Eu^{3+}. It shows that the rate constant for the intermolecular transfer in moist acetone for aromatic ketones without substituents in the benzene rings is an order of magnitude higher in the case of ketones with the lowest triplet state of the n,π^* type compared with ketones in which this state is of the π,π^* type. The introduction of electron-accepting substituents into the benzene rings (in our case halogens) greatly decreases the value of k_t.

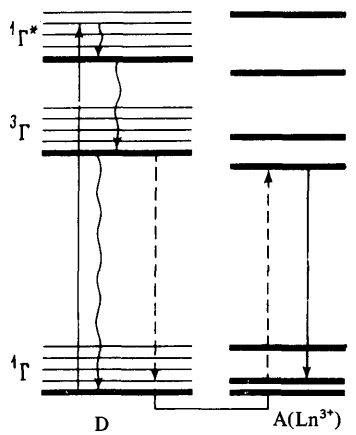


Figure 5. Schematic illustration of the electronic levels in the energy transfer from organic molecules in the triplet state ($^3\Gamma$) to lanthanide ions.

Table 10. The rate constants for the intermolecular energy transfer from the triplet state of ketones to $Eu(NO_3)_3$ in moist acetone at 293 K (according to the data of Ermolaev and Tachin[74] and Morina Sveshnikova[75]).

Ketone	Type and height of $^3\Gamma$ level, cm^{-1}	$10^{-7}k_t$, litre $mole^{-1}$ s^{-1}	Method
Acetophenone	n,π^*; 25 800	20	TT transfer*
Benzophenone	n,π^*; 24 250	60	ditto
γ-Benzoylpyridine	n,π^*; 23 000	30	»
4-Chloro-4′-methoxybenzophenone	n,π^*; 23 500	15	»
4-Bromobenzophenone	n,π^*; 23 600	3.4	»
4-Chlorobenzophenone	n,π^*; 24 000	2.0	»
4,4′-Dichlorobenzophenone	n,π^*; 24 000	1.3	»
Decafluorobenzophenone	n,π^*; 24 700	0.6	»
Methyl-2-naphthylketone	π,π^*; 20 800	1.2	i.r.**
4-Phenylbenzophenone	π,π^*; 21 225	0.9	»

*The method based on the competition with the exothermic triplet–triplet energy transfer to the organic acceptor molecule.

**The method of flash photoexcitation based on the influence of Eu^{3+} on the rate of decay of the triplet–triplet absorption in the evacuated solution.

Measurements of the rate constants for the energy transfer from aromatic ketones in the triplet state to different lanthanide ions in moist acetone at 293 K showed that the rate constant for the exothermic energy transfer varies within a range of 1–1.5 orders of magnitude and is in all cases more than 10 times smaller than the rate constant for diffusion in acetone. The attempt to find a correlation between the values of k_t and the overlap integrals of the phosphorescence spectra of the ketone donors with the absorption spectra of the lanthanide ions was unsuccessful[74]. The situation was complicated even further by studies of the influence of solvents and temperature on k_t.[40,77,81] It was established that k_t decreases on passing to solvents characterised by higher Gutmann[24] donor numbers *DN*. k_t in moist acetone, methanol and acetonitrile increases with increase of temperature. Furthermore, Sveshnikova et al.[77] established that, in solvents with low and moderate values of *DN*, there is both intermolecular diffusional and intramolecular energy transfer between aromatic ketones and lanthanide ions. The existence in solution of lanthanide complexes of aromatic ketones is indicated unambiguously by the dependence of the quenching of the luminescence sensitised by ketones on the concentration of the organic triplet energy acceptor. Instead of a straight line of the Stern–Volmer type, which obtains for purely intermolecular transfer, a curve is obtained; this is a result of the summation of two straight lines with different slopes. Examples of such relations are illustrated in Fig. 6 for the quenching by *trans*-stilbene of the luminescence of europium sensitised by 4-ethoxy-4′-methoxybenzophenone.

Scheme I

	Expression for the rate of the process	
$^1K + h\nu_{exc} \rightarrow {}^1K^* \rightsquigarrow {}^3K$	I^{I}_{exc}	(I–1)
$[^1K - Ln^{3+}] + h\nu_{exc} \rightarrow [^1K^* - Ln^{3+}] \rightarrow [^3K - Ln^{3+}]$	I^{II}_{exc}	(I–2)
$^3K \rightsquigarrow {}^1K$	k'_D	(I–3)
$^3K + {}^3O_2 \rightarrow {}^1K + {}^1O_2$	$k_t^{O_2}[O_2]$	(I–4)
$^3K + Ln^{3+} \rightarrow [^3K - Ln^{3+}]$	$k_t\,[Ln^{3+}]$	(I–5)
$^3K + {}^1A \rightarrow {}^1K + {}^3A$	$k_t^{TT}\,[^1A]$	(I–6)
$^3K + [^1K - Ln^{3+}] \rightarrow {}^1K + [^3K - Ln^{3+}]$	$k_t^{TT}\,[^1K - Ln^{3+}]$	(I–7)
$[^3K - Ln^{3+}] \rightarrow {}^3K + Ln^{3+}$	k'_{dis}	(I–8)
$[^3K - Ln^{3+}] \rightarrow [^1K - (Ln^{3+})^*]$	ω_t	(I–9)
$[^3K - Ln^{3+}] \rightarrow [^1K - Ln^{3+}]$	ω_{phch}	(I–10)
$[^3K - Ln^{3+}] + {}^1A \rightarrow [^1K - Ln^{3+}] + {}^3A$	$k_t^{TT}\,[^1A]$	(I–11)
$[^3K - Ln^{3+}] + {}^3O_2 \rightarrow [^1K - Ln^{3+}] + {}^1O_2$	$k_t^{O_2}[O_2]$	(I–12)
$[^1K - (Ln^{3+})^*] \rightarrow {}^1K + (Ln^{3+})^*$	k_{dis}	(I–13)
$(Ln^{3+})^* \rightarrow Ln^{3+} + h\nu_{s.l.}$	k_i	(I–14)
$(Ln^{3+})^* \rightsquigarrow Ln^{3+}$	k_D	(I–15)

* ^1K, $^1K^*$, and ^3K denote respectively the organic molecule of the ketone donor in the singlet ground state, the lowest singlet excited state, and the lowest triplet state respectively and ^1A, $^1A^*$, and ^3A are the corresponding quantities for the triplet energy acceptor molecule—the quenching agent for the ketone-sensitised luminescence of the lanthanide ions.

The relations illustrated in Fig. 6 are described approximately within the framework of Scheme I: (a) in the non-excited state of the solution of ketones and lanthanide ions, there is an equilibrium between the ketone–Ln^{3+} complexes $[^1K–Ln^{3+}]$ and solvated ketones (^1K) and we have $[^1K]+[^1K–Ln^{3+}] = C_K$, where C_K is the overall concentration of the ketone in solution. Under the experimental conditions, $[^1K–Ln^{3+}] \ll [Ln^{3+}]$; (b) the energy transfer from the triplet ketone to the lanthanide ion can take place either within the complex with a first-order rate constant ω_t (s^{-1}) when light is absorbed by the complex (I^{II}_{exc}) or

intermolecularly in the encounter between the triplet ketone and the lanthanide ion or the complex when light is absorbed by the free ketone (I^{I}_{exc}).

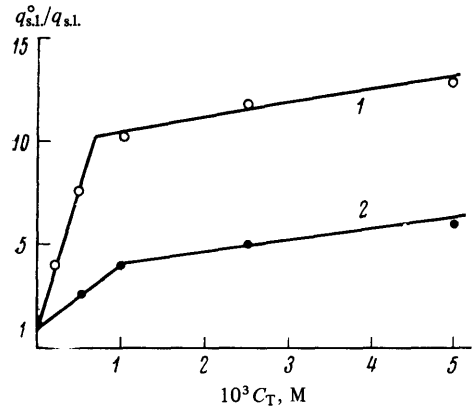


Figure 6. The quenching of the 4-ethoxy-4'-methoxybenzophenone-sensitised (C = 0.01 M) Eu^{3+} luminescence by *trans*-stilbene (concentration C_T) in acetone without O_2 at 293 K; λ_{exc} = 365 nm; Eu^{3+} concentration (M): 1) 0.0128; 2) 0.05.

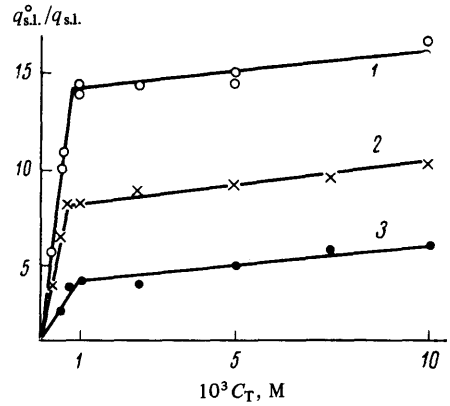


Figure 7. The influence of temperature on the quenching of the 4-methoxybenzophenone-sensitised (C = 0.01 M) Eu^{3+} luminescence (C = 0.05 M) by *trans*-stilbene in acetonitrile at different temperatures (K): 1) 233; 2) 273; 3) 293.

We shall now consider the concentration dependence of the intensity of the sensitised luminescence $I_{s.l.}$ which follows from Scheme I. The ratio of I^{I}_{exc} and I^{II}_{exc} depends on the concentrations of the complexes and the free ketone in solution and their extinction coefficients at the wavelength of the exciting light. k'_d is the rate constant for the deactivation of the triplet ketone in the de-aerated solution (I-3); (I-4) represents the quenching of the triplet ketone by oxygen; (I-5) is the reaction involving the incorporation of the triplet ketone in the first coordination sphere of the ion; (I-6) and (I-11) represent the exothermic energy transfer from the triplet ketone to the triplet energy acceptor introduced into the solution, the rate of this process being limited by diffusion ($k^{TT}_t = k_d$); (I-7) is the energy transfer from the triplet ketone to the complex; (I-8) is the dissociation of the triplet complex into the triplet ketone and the non-excited lanthanide ion. The very small temperature dependence of the quenching of the luminescence of the complexes shows that the dissociation process may be neglected compared with the intramolecular energy transfer [ω_t, (I-9)] and the photochemical reaction within the complex [ω_{phch}, (I-10)], i.e. $\omega_t + \omega_{phch} \gg k'_{dis}$. The quenching of the luminescence of the complex by oxygen (I-12) is also not observed and $\omega_t + \omega_{phch} \gg k'_{dis} + k^{O_2}_t[O_2]$. The lifetime of the luminescent lanthanide ion is long and there is sufficient time for the dissociation of the complex (I-13). Reactions (I-14) and (I-15) correspond to the processes involving the emission of the sensitised luminescence and the degradation of the electronic excitation energy into heat.

Having chosen the experimental conditions, it is possible to simplify the scheme by neglecting a number of processes. By carrying out experiments in de-oxygenated solutions or by establishing a sufficiently high concentration of Ln^{3+}, it is possible to neglect processes (I-3) and (I-4) compared with (I-5) and (I-6). Furthermore, at a relatively low ketone concentration one can disregard process (I-7) involving energy transfer to the complexes, so that

$$k_t[Ln^{3+}] + k^{TT}_t[^1A] \gg k'_D + k^{O_2}_t[O_2] + k^{TT}_t[^1K - Ln^{3+}].$$

Under the conditions formulated, namely

$$\omega_t + \omega_{phch} \gg k'_{dis} + k^{O_2}_t[O_2]$$

and

$$k_t[Ln^{3+}] \gg k'_D + k^{O_2}_t[O_2] + k^{TT}_t[^1K - Ln^{3+}],$$

the expression for $q_{s.l.}$ assumes the following form:

$$q_{s.l.} = \frac{I^{I}_{exc}}{I_{exc}} \cdot \frac{k_i}{k_i + k_d} \cdot \frac{k_t[Ln^{3+}]}{k_t[Ln^{3+}] + k^{TT}_t[^1A]} \cdot \frac{\omega_t}{\omega_t + \omega_{phch} + k^{TT}_t[^1A]} + \frac{I^{II}_{exc}}{I_{exc}} \cdot \frac{k_i}{k_i + k_d} \cdot \frac{\omega_t}{\omega_t + \omega_{phch} + k^{TT}_t[^1A]},$$

where $I_{exc} = I^{I}_{exc} + I^{II}_{exc}$. The experimental ratio of the intensity of the sensitised luminescence in the absence of quenching agent $q^{0}_{s.l.}$ to the intensity in its presence at a concentration [^{1}A] is given by the following expression:

$$\frac{q^{0}_{s.l.}}{q_{s.l.}} = \frac{\left(1 + \frac{k^{TT}_t}{\omega_t + \omega_{phch}} \cdot [^1A]\right)\left(1 + \frac{k^{TT}_t[^1A]}{k_t[Ln^{3+}]}\right)}{\left(1 + \frac{I^{II}_{exc}}{I^{I}_{exc} + I^{II}_{exc}} \cdot \frac{k^{TT}_t[^1A]}{k_t[Ln^{3+}]}\right)}. \quad (14)$$

Bearing in mind that $\omega_t + \omega_{phch} \gg k_t(Ln^{3+})$, one can examine two limiting quenching agent concentration ranges. At low quenching agent concentrations, where $k^{TT}_t[^1A]/k_t[Ln^{3+}] < 1$ and bearing in mind that $k^{TT}_t[^1A] \ll \omega_t + \omega_{phch}$ and $I^{I}_{exc} \simeq I^{II}_{exc}$, Eqn. (13) can be replaced by the approximate expression

$$\frac{q^{0}_{s.l.}}{q_{s.l.}} \simeq 1 + \frac{I^{I}_{exc}}{I^{I}_{exc} + I^{II}_{exc}} \cdot \frac{k^{TT}_t[^1A]}{k_t[Ln^{3+}]}. \quad (15)$$

This expression simplifies still further when the concentration of stable complexes in the ground state is low, so that $I^{I}_{exc} \gg I^{II}_{exc}$. Then

$$\frac{q^0_{s.l.}}{q_{s.l.}} = 1 + \frac{k_t^{TT}[^1A]}{k_t[Ln^{3+}]}. \quad (16)$$

On the other hand, at high quenching agent concentrations, we have $I^{I}_{exc} \simeq I^{II}_{exc}$ and $k_t^{TT}[^1A]k_t[Ln^{3+}] \gg 1$. We then obtain a linear variation with $[^1A]$:

$$\frac{q^0_{s.l.}}{q_{s.l.}} = \frac{I^{I}_{exc} + I^{II}_{exc}}{I^{II}_{exc}}\left(1 + \frac{k_t^{TT}}{\omega_t + \omega_{phch}}[^1A]\right). \quad (17)$$

The intercept which this straight line makes on the ordinate axis makes it possible to estimate $(I^{I}_{exc} + I^{II}_{exc})/I^{II}_{exc}$, i.e. the reciprocal of the fraction of light absorbed by the complexes $[^1K-Ln^{3+}]$ in solution at a given concentration of lanthanide ions and therefore permits the estimation of their stability constants.

Since the rate constant for the exothermic triplet energy transfer is equal to the diffusional constant, $k_t^{TT} = k_d$, and is calculated from the Vavilov–Debye formula[82,83] $k_t^{TT} = k_d = 8RT/3000\eta$ (litre mole^{-1}s^{-1}), the slopes of the linear relations (15)–(17) corresponding to low values of $[^1A]$ make it possible to determine the rate constant for the intermolecular energy transfer from the triplet ketone to the lanthanide ion (k_t), while the slope corresponding to high values of $[^1A]$ permits the determination of the sum of the constants for the intramolecular energy transfer (ω_t) and the photochemical reaction within the complex (ω_{phch}). Knowing the yield of the photochemical reaction[76], it is possible to find ω_t from the sum. The values of k_t, ω_t, and the stability constants β of the complexes $[^1K-Ln^{3+}]$ obtained in the above investigation are listed in Table 11.

Scheme I differs from the schemes usually employed for the description of energy transfer by the allowance for the complex-formation reaction with the lanthanide ions involving the ground and triplet states of the ketone. The validity of the hypothesis of the simultaneous occurrence of two processes involving the formation of ketone–Ln^{3+} complexes is confirmed by the following findings: (1) the relations between $q^0_{s.l.}/q_{s.l.}$ and the concentration of *trans*-stilbene presented in Fig. 6 for various ratios of the concentrations of the ketone and the lanthanide ion; (2) the variation of the intercept of the low-slope straight lines describing the dependence of $q^0_{s.l.}/q_{s.l.}$ on the concentration of the quenching agent (trans-stilbene) with increased ratio of the concentrations of Eu^{3+} and the ketone (Fig. 6); (3) the decrease of $q_{s.l.}$ following the introduction into the solution of salts of gadolinium(III), which does not quench triplet states but is capable of forming stable complexes with the ketone and competing in this respect with Eu^{3+} ions. The presence of gadolinium ions hardly influences the slope of the two straight lines which describe approximately the variation of $q^0_{s.l.}/q_{s.l.}$ with the concentration of *trans*-stilbene.

The validity of the assumption made in the derivation of Eqns. (12)–(16) that one can neglect the dissociation of complexes of the type $[^3K-Ln^{3+}]$, i.e. that $\omega_t + \omega_{phch} \gg k'_{dis}$, where k'_{dis} is the rate constant for the dissociation of the complex, is confirmed by the weak influence of a change of temperature on the slope of the low-slope straight line in Fig. 7.

A study was made of the influence of electron-donating and electron-accepting substituents in ketones on the rate constants of the intramolecular and intermolecular energy transfer to lanthanide ions. The values of k_t and ω_t are listed in Tables 10 and 11. ω_t increases when electron-donating groups (OCH_3, OC_2H_5)¶ are introduced into the benzene rings of benzophenone and falls when electron-accepting groups (Br, Cl) are introduced. Substituents have a similar effect also on k_t, but the amplitude of the relative changed in k_t is smaller under these conditions. It has also been shown that k_t and ω_t increase with decrease of the electron-donating capacity of the solvent (see Table 11). Unfortunately the solvents employed in the investigation contain an admixture of water, which naturally complicated the observed picture. The admixture of water has a particularly marked influence in the study of energy transfer in solvents which are weak electron donors.

Valuable information was obtained from the study of the temperature dependence of k_t. This phenomenon was investigated in greatest detail in acetone and acetonitrile for 4-ethoxy-4'-methoxybenzophenone and 4-methoxybenzophenone as the energy donors and Eu^{3+} as the energy

Table 11. Intermolecular (k_t, litre mole^{-1}s^{-1}) and intramolecular (ω_t, s^{-1}) rate constants for energy transfer from the triplet molecules of aromatic ketones to Eu^{3+} ions in various solvents. Estimation of the activation energies for the transfer process (ΔE, kcal mole^{-1}) and the stability constants of the $[^1K-Eu^{3+}]$ complexes (β_1, litre mole^{-1}) at 293 K (according to the data of Sveshnikova et al.[77]).

Energy donor	Methanol DN ~20; ε=32.6			Acetone (moist) DN=17; ε=20.7				Acetonitrile (moist) DN=14; ε=37.5				Acetic anhydride DN=10; ε=20.7			
	$10^{-7}\cdot k_t$	ΔE	β_1	$10^{-7}\cdot k_t$	ΔE	$10^{-7}\cdot\omega_t$	β_1	$10^{-7}\cdot k_t$	ΔE	$10^{-7}\cdot\omega_t$	β_1	$10^{-7}\cdot k_t$	ΔE	$10^{-7}\cdot\omega_t$	β_1
4-Ethoxy-4'-methoxybenzophenone	5.5	3.0	<0.2	13	3.2	250	~5	nc.	—	600	>50	nc.	—	350	>50
4-Methoxybenzophenone	3.0	3.2	<0.2	7	2.2	40	~0.6	24	2.3	120	~5	—	—	—	—
Acetophenone	5.0	—	<0.2	20	2.0	nc*	<0.2	—	—	—	—	37	—	34	~5
4-Bromobenzophenone	1.3	—	<0.2	3.4	1.8	nc.	<0.2	14	—	8	~1.4	—	—	—	—
4,4'-Dichlorobenzophenone	—	—	—	1.3	1.4	nc.	<0.2	4.6	1.2	3	~0.4	—	—	—	—

*nc = no complex.

¶Stable lanthanide complexes with stronger electron donors—aromatic acid anions ($Ar-COO^-$)[84] and alkoxyacetophenones[85]—are also observed in solvents characterised by a higher donor number (methanol)[84].

acceptor. With increase of temperature, k_t rises exponentially and the calculated activation energies for the formation of a complex of the triplet ketone and Eu^{3+} are 1–3 kcal mole^{-1} (Table 11).

Presumably the rate constant k_t for the diffusional energy transfer between the triplet ketone and the lanthanide ion is described by the following expression:

$$k_t = A e^{-\frac{\Delta E}{kT}},$$

where the coefficient A is proportional to the number of encounters between the triplet ketone molecules and the lanthanide ions, i.e. to k_d, and to the duration of each encounter Δt_{enc}, i.e. $A = k_d \Delta t_{enc}$. Since Δt_{enc} is inversely proportional to k_d, A will not vary as k_d increases and can therefore be regarded as independent of temperature. The second factor characterises the probability of the incorporation of the triplet ketone in the first coordination sphere of the lanthanide ion during the encounter. It increases exponentially with increase of temperature. The values of ΔE obtained diminish with decrease of the electron-donating capacity of the ketone. This may be due to the change in the bonding energy between the ketone and the water molecules present in solution. Experiments on energy transfer uncomplicated by the presence of an admixture of water are extremely desirable.

Thus experiment showed that the rate constant for the intermolecular energy transfer from aromatic ketones to lanthanide ions in solution is determined by the chemical incorporation of the triplet ketone molecule in the first coordination sphere of the lanthanide ion and not by the physical energy transfer process. The rate of such incorporation depends on the chemical properties of the triplet state of the ketone. It is much higher for triplet ketones with the lowest level of the n,π^* type compared with ketones in which this level is of the π,π^* type, and increases following the introduction of electron-donating substituents into the benzene rings of the ketones (Table 10).

The study of the dependence of the rate constant for the intermolecular energy transfer from aromatic ketones with n,π^* and π,π^* triplet levels on the atomic number of the lanthanide ion, undertaken in a number of investigations[74–77], showed that, despite the considerable differences between the absolute values of k_t for transfer from the n,π^* and π,π^* levels, the relative changes in k_t in the series of lanthanide ions take place approximately in parallel (see Fig. 8). We believe this to be an additional confirmation of the hypothesis that k_t is mainly determined by the rate of incorporation of the triplet ketone in the first coordination sphere of the lanthanide ion and that this rate varies appreciably in the series of lanthanides.

The values of k_t cannot be unambiguously related to the rate of incorporation in the complex only for very low values of ω_t, which are observed for a highly endothermic energy transfer (to Gd^{3+} for ketones with the $^3\Gamma$ state of the n,π^* type and to Gd^{3+}, Dy^{3+}, Tb^{3+}, etc. for ketones with the $^3\Gamma$ state of the π,π^* type), since in the energy transfer method the indicator is the subsequent quenching of the triplet in the complex. In the interaction with Gd^{3+} and other ions, this quenching cannot occur for energetic reasons and there may be sufficient time for the dissociation of the complex $[^3K–Gd^{3+}]$.

With increase of temperature, there is also an increase of the relative concentration of stable ketone–lanthanide ion complexes in the ground state in acetone and acetonitrile. This is consistent with Matovich and Suzuki's observation[58] that the temperature dependence of the energy transfer reaction is characteristic of an endothermic process. We believe that the observed type of temperature dependence of the concentration of complexes of the type $[^1K–Ln^{3+}]$ in acetone and acetonitrile is associated with the competition between various ligands in the first coordination sphere of the lanthanide ion, in particular with the competition between the aromatic ketone and the dissolved water as a ligand.

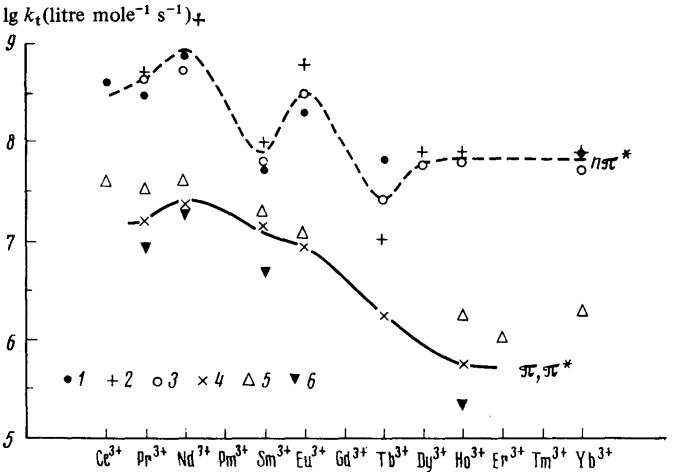


Figure 8. Dependence of the logarithms of the rate constants for energy transfer from aromatic ketones in the triplet state to lanthanide ions on the atomic number of the latter in moist acetone at 293 K: 1) acetophenone; 2) benzophenone; 3) benzoylpyridine; 4) 4-phenylbenzophenone; 5) methyl 2-naphthyl ketone; 6) 9-anthryl methyl ketone. For ketones with the lowest $^3\Gamma$ state of the n,π^* type, the values of k_t were measured by the method of competing lanthanide ions with energy transfer to Eu^{3+}; for ketones with the $^3\Gamma$ state of the π,π^* type, the flash photoexcitation method was used.

2. Energy Transfer from Lanthanide Ions to Organic Molecules with Excitation of the Triplet Level

Vavilov and Sevchenko[86] did not observe a decrease of the luminescence yield of an alcoholic solution of Sm^{3+} in the presence of typical fluorescence quenching agents: aniline, nitrobenzene, resorcinol, KI, etc. However, recently Aleksandrov et al.[87] and Kleinerman[88] noted a decrease in the decay time and in the intensity of the Eu^{3+} luminescence in solution after the addition of aromatic hydrocarbons, whose triplet level lies below the resonance level ($^5D_0$) of the Eu^{3+} ion. Subsequently Ermolaev and Tachin[40,48,49,81,89,92] made a detailed study of this phenomenon and showed that it is due to the non-radiative energy transfer from the lanthanide ions (Tb^{3+}, Eu^{3+}, and Dy^{3+}) to the organic molecules with excitation of the latter to the triplet state. The energy transfer takes place via the exchange resonance mechanism. The luminescence of the

Eu^{3+} ($^5D_0$) ion, which exhibits the maximum electron affinity, is quenched in some cases also via the electron transfer mechanism[89]. Thus two processes are responsible for the quenching:

$$^m(Ln^{3+})^* + {}^1A \rightarrow {}^n(Ln^{3+}) + {}^3A, \quad (18)$$

$$^m(Ln^{3+})^* + {}^1A \rightarrow {}^k(Ln^{3+}) + {}^2A^- . \quad (19)$$

The electron energy level diagram for reaction (18) is illustrated in Fig. 9. The energy transfer process is not accompanied by the internal conversion of some of the electronic excitation quanta. This was demonstrated by Tachin and Ermolaev[90], who investigated the energy transfer from $Tb^{3+}(^5D_4)$ to Eu^{3+} in acetone via methyl 2-naphthyl ketone as an intermediate and showed that one excited Eu^{3+} ion corresponds to one quenched Tb^{3+} ion.

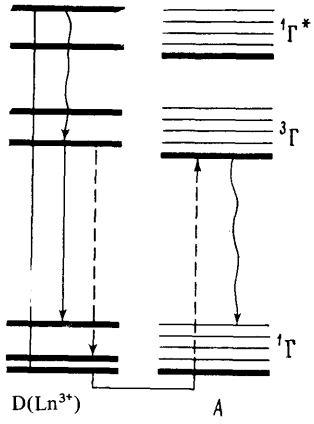


Figure 9. Schematic illustration of the electronic levels in the energy transfer from lanthanide ions to organic molecules with excitation of the latter to the triplet state.

Table 12 lists the values of[89] k_t (in moist acetone) for energy transfer from lanthanide ions to various aromatic molecules. It shows that (1) k_t is much lower than the diffusion rate constant and (2) the k_t for transfer to molecules with substituents (–$COCH_3$, >N, etc.) capable of forming coordinate bonds with lanthanide ions are higher by 1–2 orders of magnitude than for energy transfer to molecules of unsubstituted aromatic hydrocarbons. The k_t for energy transfer to aromatic ketones are close to the corresponding values for energy transfer from aromatic ketones ($^3\pi,\pi^*$) to lanthanide ions (cf. Tables 10 and 12 and Fig. 8), provided that the reaction is exothermic in both cases. The closeness of the observed values of k_t demonstrates the complexity of the kinetics of these processes. Presumably the rate-limiting step of the energy transfer from lanthanide ions to aromatic ketones as well as that in the reverse transfer is the incorporation of the aromatic ketone in the first coordination sphere of the lanthanide ion. The difference is that, in the energy transfer from the lanthanide ion, the aromatic ketone in the ground singlet state is incorporated in the hydration shell of the excited lanthanide ion, while in the energy transfer from the triplet ketone the latter is incorporated in the inner solvation shell of the non-excited lanthanide ion. The experimental values of k_t for both types of transfer do not differ greatly, in agreement with the weak influence of the excitation of the shielded $4f$ shells on the chemical properties of lanthanide ions and also with the insignificant changes in the electron-donating properties of aromatic ketones on excitation to the π,π^* triplet state relative to the ground state[91].

Table 12. The rate constants for energy transfer from lanthanide ions to organic molecules with transition of the latter to the triplet state in moist acetone [$k_d = 2.1 \times 10^{10}$ litre mole^{-1}s^{-1}; in air; 293 K (data of Ermolaev and Tachin[89]); E_A = energy of the $^3\Gamma$ state of the energy acceptor].

Quenching agent	E_A, cm^{-1}	k_t^*, litre mole^{-1} s^{-1}
Eu^{3+} donor (energy of $^5D_0$ emission level 17 200 cm^{-1})		
1-Anthryl methyl ketone	15 160	$4.7 \cdot 10^6$
Acridine	15 840	$1.2 \cdot 10^6$
Anthracene	14 900	$1.0 \cdot 10^5$***
Methyl 2-naphthyl ketone	20 800	$1.0 \cdot 10^3$
NN-Dimethylaniline	26 600	$5.3 \cdot 10^5$**
Tb^{3+} donor (energy of $^5D_4$ emission level 20 500 cm^{-1})		
Methyl 2-naphthyl ketone	20 800	$2.1 \cdot 10^6$
Acridine	15 840	$1.6 \cdot 10^6$
Fluorenone	19 200	$1.0 \cdot 10^6$
1-Naphthoic acid	20 200	$8.5 \cdot 10^5$
Anthracene	14 900	$1.0 \cdot 10^5$
Dy^{3+} donor (energy of $^4F_{9/2}$ emission level 20 800 cm^{-1})		
Fluorenone	19 200	$8.9 \cdot 10^5$
Methyl 2-naphthyl ketone	20 800	$7.6 \cdot 10^5$

* Accuracy of the measurements of k_t ~ 20–30%.
** Quenching via the electron transfer mechanism.
*** An error was made in the study of Ermolaev and Tachin[89]. The corrected value is quoted here.

Ermolaev and Tachin[92] made a comparative study of the influence of temperature and the solvent on k_t for energy transfer from Tb^{3+} to 9-anthryl methyl ketone (AMK) and to anthracene (A). The results obtained are listed in Table 13, showing that k_t for the transfer from Tb^{3+} to the ketone decreases by more than 2 orders of magnitude with increase of the electron-donating capacity of the solvent molecules, while k_t for the transfer to anthracene depends little on the electron-donating capacity of the solvent. A significant difference between these two examples is also observed in the temperature variation of k_t. In the first case, involving energy transfer to the ketone, the process has an activation energy which increases with the increase of the donor number of the solvent and decreases to zero for solvents with a high electron-donating capacity. On the other hand, k_t for energy transfer to anthracene is independent of temperature, except in dimethyl sulphoxide. In solvents with a high electron-donating capacity, the values of k_t for energy transfer to 9-anthryl methyl ketone and anthracene agree within the limits of experimental error. Evidently the anthracene molecule cannot penetrate the first coordination sphere of the lanthanide ion and k_t corresponds in this case to energy transfer to the acceptor molecule in the second coordination sphere. Similarly the 9-anthryl methyl ketone molecule likewise does not penetrate the first coordination sphere in solvents with a high electron-donating

capacity. The relatively high rate constant for energy transfer to the ketone in solvents with a low electron-donating capacity (which is at least 3 orders of magnitude lower than the diffusion-limited rate constant) undoubtedly corresponds to the incorporation of the ketone in the first coordination sphere of the excited Tb^{3+} ion.

Table 13. The rate constants for energy transfer (k_t) from Tb^{3+} ($^5D_0$ = 20 500 cm^{-1}) to 9-anthryl methyl ketone (AMK) ($^3\Gamma$ = 15 160 cm^{-1}) and anthracene (A) ($^3\Gamma$ = 14 900 cm^{-1}) in liquid dried solutions at 293 K. The estimated rates of incorporation of AMK in the first coordination sphere of Tb^{3+} [$k_{inc} = k_t(AMK) - k_t(A)$] and the activation energies for this reaction (ΔE_{inc}).

Solvent	DN, kcal mole^{-1}	τ_0, ms	Acceptor: 9-anthryl methyl ketone, k_t, litre mole^{-1} s^{-1}	Acceptor: Anthracene, k_t, litre mole^{-1} s^{-1}	Acceptor: Anthracene, ΔE, kcal mole^{-1}	k_{inc}, litre mole^{-1} s^{-1}	ΔE_{inc}, kcal mole^{-1}
Acetonitrile	14.1	1.7	$1.0\cdot10^7$	$1.4\cdot10^5$	0	$1.0\cdot10^7$	3.0
Acetone	17.0	1.7	$3.4\cdot10^6$	$1.8\cdot10^5$	0	$3.3\cdot10^6$	3.2
			$4.0\cdot10^5$*	$1.9\cdot10^5$	—	—	—
Ethyl acetate	17.1	1.8	$1.9\cdot10^6$	—	—	—	4.1*
Propanol	—	1.35	$3.2\cdot10^5$	$9.5\cdot10^4$	0	$2.0\cdot10^5$	4.8
Methanol	—	1.35	$2.1\cdot10^5$	$1.1\cdot10^5$	0	$1.0\cdot10^5$	5.0
Pyridine	33.1	1.3	$1.9\cdot10^5$	$1.1\cdot10^5$	0	$8.0\cdot10^4$	5.5
Trimethyl phosphate	23.0	2.7	$3.2\cdot10^4$	$3.2\cdot10^4$	0	$<10^3$	—
Tributyl phosphate	23.7	2.4	$4.2\cdot10^4$	$4.2\cdot10^4$	0	$<10^3$	—
			$(4.2\cdot10^4)$*	$(4.2\cdot10^4)$*	0	—	—
Dimethyl sulphoxide	28.9	2.6	$7.2\cdot10^4$	$7.2\cdot10^4$	2.0***	$<10^3$	—

* Moist solution.
** Activation energy $\Delta E[k_t(AMK)]$.
*** Activation energy $\Delta E[k_t(AMK)] = \Delta E[k_t(A)]$.

The observed activation energies ΔE were calculated from the variation of $\ln[k_t(AMK)-k_t(A)]$ with the reciprocal of temperature and probably correspond to the activation energy for the dissociation of the solvent molecule from the first coordination sphere of the lanthanide ion. The last column of Table 13 lists the rates of incorporation of the ketone in the first coordination sphere of the Tb^{3+} ion in the $^5D_4$ state, calculated from the formula $k_{inc} = k_t(AMK) - k_t(A)$. In dimethyl sulphoxide, there is probably an ordered arrangement of the molecules in the second coordination sphere and the activation energy for incorporation in the second coordination sphere is observed.

We believe that the findings described above demonstrate quite convincingly the considerable scope of the energy transfer method in the study of reversible and dynamic complex formation reactions between organic molecules and lanthanide ions in solution. The following observations have been made with the aid of this method: (1) a new type of ion pairs comprising anionic dyes and lanthanide ions in solutions has been discovered; (2) equilibrium in solvents with a low electron-donating capacity between aromatic ketone–lanthanide ion complexes and solvated ketones and lanthanide ions has been demonstrated and the stability constants of the complexes have been estimated; (3) a number of conclusions have been drawn concerning the dynamics of the incorporation of triplet ketones in the inner coordination sphere of non-excited lanthanide ions and the activation energies for this process have been determined; (4) information has been obtained about the incorporation of a non-excited aromatic ketone in the inner solvation shells of excited lanthanide ions and the activation energies for this process in various solvents have been determined.

The experimental technique of studies on complex formation by the energy transfer method is in the main simple and does not require expensive apparatus. In most cases, it comprises the usual photoelectric apparatus for the measurement of the intensity and rate of decay of luminescence. Such apparatus and the required techniques have been described in a recently published translation of Parker's book[93]. More complex flash photoexcitation methods have been described by Shakhverdov[94] and Boag[95] and in the monograph by Calvert and Pitts[96], and laser photoexcitation methods are given in the paper by Porter and Topp[97]. We are certain that the energy transfer method will soon become the normal procedure in chemical laboratories dealing with problems of coordination chemistry.

ADDED IN PROOF

During the preparation of the review for the press, a detailed survey of the processes involving the sensitisation and quenching of the luminescence of coordination compounds (mainly those of transition metal ions) was published by Balzani et al.[98] Their survey and our reviews in this journal complement one another successfully.

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