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Coordination Chemistry Reviews
159 (1997) 55–74

COORDINATION CHEMISTRY REVIEWS

Quenching of triplet states of organic compounds by 1,3-diketonate transition-metal chelates in solution. Energy and/or electron transfer

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Received 22 December 1995

Contents

Abstract

1,3-Diketonate transition-metal chelates are shown to be excellent model compounds to study the interaction between excited states of organic compounds and coordination complexes in solution. They are particularly useful for studying both energy- and electron-transfer quenching. The results of laser flash and steady-state photolysis measurements for quenching of triplet states of organic compounds by acetylacetonates (acac) and hexafluoroacetylacetonates (hfac) of transition metals (Cu(II), Ni(II), Cr(III), and Fe(III)) and lanthanides (Sm(III), Eu(III), Gd(III), Tb(III), and Dy(III)) and Mg(II) in solution (acetonitrile and benzene) are reviewed. No sensitized luminescence (except for 1,3-diketonates of some lanthanides) was found. In addition, no short-lived transients were found that could be ascribed to sensitized excited states of 1,3-diketonate complexes or to electron-transfer intermediates. However, much useful indirect evidence concerning the nature of the triplet quenching was obtained. The methodology involved first measuring the quenching rate constants of a series of organic triplet states by selected 1,3-diketonate complexes and then analyzing the correlations between these rate constants and the standard free-energy changes for energy or electron transfer. With a classical framework for energy and electron transfer, these correlations were

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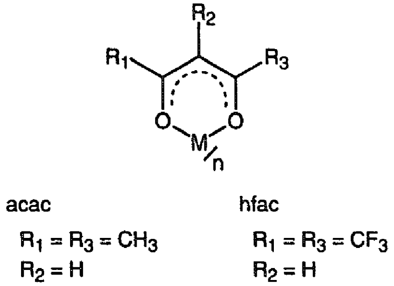
PII S0010-8545(96)01306-9

used to evaluate appropriate intrinsic barriers and transmission coefficients for both processes. The quenching data were interpreted in terms of energy and electron transfer alone or in terms of both as competing processes. It was shown that the quenching of most of the organic triplet states by 1,3-diketonates of Ni(II), lanthanides, and Mg(II) (as well as $Cr(acac)_3$ and $Fe(acac)_3$) was adequately described by the energy transfer to the ligand-localized triplet states or to the metal-centered excited dd or ff states of the complexes. The transmission coefficients of these processes were in the range of 10^{-3}, 10^{-3}–10^{-5}, and 10^{-6}, respectively. Quenching by $Cu(acac)_2$ was suggested to occur mainly by electron transfer, whereas quenching by $Cu(hfac)_2$ was shown to involve energy transfer to the ligand-localized triplet state in competition with electron transfer from the organic triplet states to the Cu(II) complex. An additional quenching process, that is electron transfer from the acetylacetonate ligand to the benzophenone triplet state, was observed for triplet states of benzophenone derivatives. The latter process led to the sensitized photochemistry of Cu(II) and Ni(II) acetylacetonates, in hydrogen-donating solvents.

Keywords: Triplet state quenching; 1,3-Diketonate transition-metal chelates; Energy transfer; Electron transfer

1. Introduction

1,3-Diketonate transition-metal chelates (ML_n) are excellent model compounds to study the interaction between excited states of organic compounds and coordination complexes in solution. With these chelates there are many possibilities for energy and electron transfer, as well as possible interplay between these processes.



The ML_n compounds have numerous low-lying electronic excited states of different orbital/spin character, making them a diverse set of potential energy acceptors [1,2]. A typical example of an energy-level diagram for these complexes is presented in Fig. 1 [2]. This variety of excited states has proven useful in studies of energy-transfer processes [2–13]. The wide range of redox potentials of ML_n compounds also makes them convenient quenchers for studies of electron-transfer processes [11–16]. Moreover, the 1,3-diketonate metal chelates exhibit physical and chemical properties that make them suitable archetypes for photochemical studies of coordination compounds in solution [1,2]. It has been shown by Chow and co-workers [2,17–22] that aromatic ketones in excited triplet states can sensitize a photoreduc-

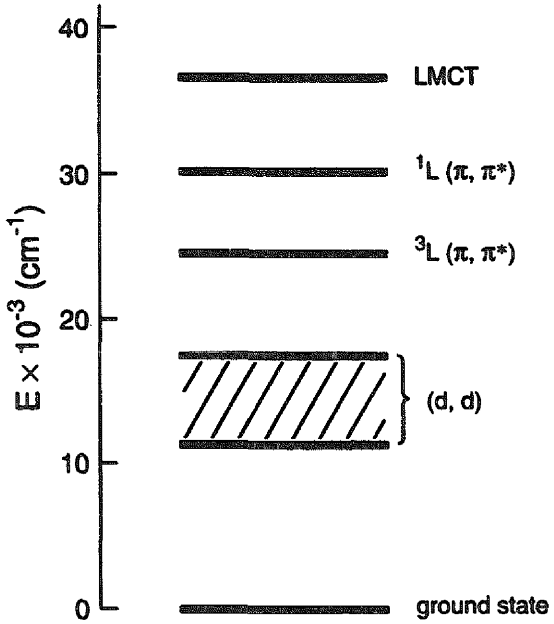


Fig. 1. Energy-level diagram of the low-lying excited states of $Cu(acac)_2$ (from [2]).

tion of copper(II) and nickel(II) 1,3-diketonates in hydrogen-donating solvents, and the electron-transfer process from acetylacetonate (acac) ligands to the benzophenone triplet state was suggested as a primary photochemical step.

Quenching of the triplet states of organic compounds by 1,3-diketonates of transition metals has been the subject of many investigations [2–22]. Since ML_n complexes do not luminesce in solution at room temperature (except for the 1,3-diketonates of some lanthanides) and since the transient absorption spectra of their excited states have not been detected, direct evidence for energy-transfer quenching has not been established experimentally. Furthermore, no short-lived transients have been found that could be ascribed to electron-transfer intermediates. In spite of this failure to observe transients directly, much useful indirect evidence concerning the nature of the quenching by ML_n complexes has been obtained. The methodology involved first measuring the rate constants, k_q, of a series of excited organic molecules being quenched by various ML_n complexes. Correlations were then analyzed between these rate constants and the standard free-energy changes for the processes in question. Since the reactions often turned out to be close to diffusion controlled, it was considered that only electron transfer and/or energy transfer were fast enough to be likely mechanisms. Thus for these reactions, the free energies of relevance were ΔG_{en} (see Eq. (5)) for energy transfer and ΔG_{el} (see Eq. (6)) for electron transfer (Rehm–Weller correlations [23]).

Correlations typical of the behavior of these reactions are illustrated in Fig. 2 by the k_q dependence on ΔG_{el} for electron-transfer quenching of aromatic singlet states.

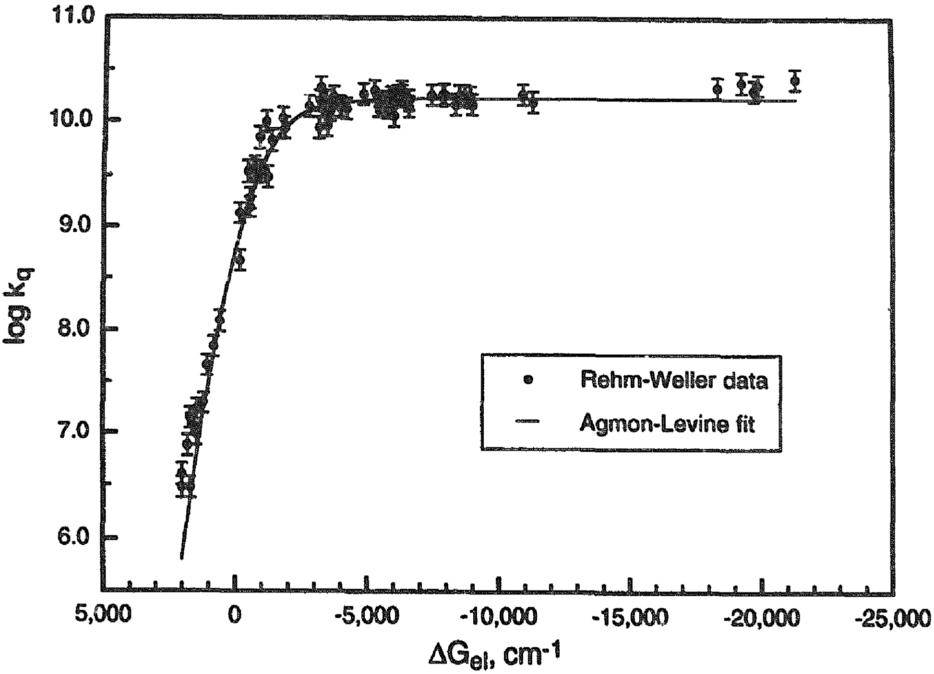
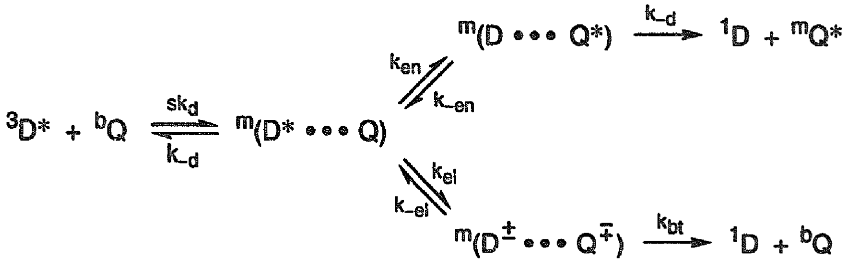


Fig. 2. Typical plot of log k_q vs. ΔG_{el} for electron-transfer quenching of excited states. Data are from [23] for organic singlet state quenching, and the analysis is from [24].

The experimental data were taken from [23] and were analyzed in detail in [24]. In the figure, it can be seen that the curve is flat, forming a plateau, when the reactions are exoergonic enough (negative values of ΔG_{el}). As the endoergonic region is approached, there is an intermediate region of the curve where its slope changes rapidly. Finally, when reactions are sufficiently endoergonic, the curve is characterized by an Arrhenius-type region where its slope is equal to $1/(2.3RT)$. Such observed correlations between log k_q and ΔG_{el} (or ΔG_{en}) can be taken as evidence for electron (or energy) transfer quenching. Treatments such as this are generally accepted and have been successfully used by various workers studying both energy- and electron-transfer quenching [7,8,23–26]. Of particular note for this review is the work of Wilkinson and co-workers on the quenching of triplet states by Cr(III) and Fe(III) 1,3-diketonates in benzene solutions [3–6,11,12,14,15].

2. Theories of the quenching mechanisms

Quenching of the triplet state of organic compounds by ML_n complexes can be interpreted according to general schemes describing energy- and electron-transfer processes:



(1)

(2)

where s is a spin statistical factor equal to [12] $m/3b$ (b and m are the spin multiplicity of the quencher and the encounter complex, respectively), k_d is the diffusion rate constant, k_{-d} is the dissociation rate constant of the encounter complex, and k_{bt} is the rate constant for back electron transfer to form the reactants in their ground states. The energy- and electron-transfer equilibria are characterized by rate constants k_{en} (k_{el}) and k_{-en} (k_{-el}) that can be treated classically [7] with the same formalism:

$$\ln(k_{en}/k_{-en}) = -\Delta G_{en}/RT \tag{3}$$

$$\ln(k_{el}/k_{-el}) = -\Delta G_{el}/RT \tag{4}$$

where ΔG_{en} and ΔG_{el} are the standard free-energy changes for the energy- and electron-transfer processes. The ΔG_{en} can be evaluated from the zero–zero transition wavenumbers ($\bar{\nu}_{0\text{-}0}$) of excited donor and quencher [14]:

$$\Delta G_{en} = -Nhc[2\bar{\nu}_{0\text{-}0}(^3\mathrm{D}^*) - \bar{\nu}_{0\text{-}0}(^m\mathrm{Q}^*)] \tag{5}$$

whereas the free-energy change for electron transfer to form the exciplex $^m(\mathrm{D}^{\pm}\cdots\mathrm{Q}^{\mp})$ can be given by [14]

$$\Delta G_{el} = F(E_{ox} - E_{red}) - E_T + \Delta w \tag{6}$$

Δw contains the Coulombic interaction energy and changes in solvation energy of the separated ions and the exciplex [11]. E_{ox} is the oxidation potential of the electron donor, E_{red} is the reduction potential of the electron acceptor, and E_T is the energy of the triplet state being quenched.

Using the steady-state approximation and confining the discussion to only one multiplicity (m) of the quencher, one can obtain from reaction schemes of Eqs. (1) and (2) for energy- and electron-transfer quenching, respectively,

$$k_q^{en} = sk_d\left[1 + \frac{k_{-d}}{k_{en}^0}\exp\left(\frac{\Delta G_{en}^{\neq}}{RT}\right) + \exp\left(\frac{\Delta G_{en}}{RT}\right)\right]^{-1} \tag{7}$$

$$k_q^{el} = sk_d\left[1 + \frac{k_{-d}}{k_{el}^0}\exp\left(\frac{\Delta G_{el}^{\neq}}{RT}\right) + \frac{k_{-d}}{k_{bt}}\exp\left(\frac{\Delta G_{el}}{RT}\right)\right]^{-1} \tag{8}$$

where $\Delta G_{en}^{\neq}$ and $\Delta G_{el}^{\neq}$ are the free energies of activation for the energy- and electron-transfer processes; k^0_{en} and k^0_{el} are the preexponential factors,

$$k_{\mathrm{en(el)}}=k^0_{\mathrm{en(el)}}\exp\left(\frac{-\Delta G^{\neq}_{\mathrm{en(el)}}}{RT}\right) \tag{9}$$

which are related to the transmission coefficients, κ, by the relation [27]

$$k^0_{\mathrm{en(el)}}=\kappa_{\mathrm{en(el)}}k_{\mathrm{B}}T/h \tag{10}$$

where k_{B} and h are the Boltzmann and the Planck constants, respectively.

The limiting value of k_{q} for sufficiently exoergonic energy or electron transfer ($k_{\mathrm{en(el)}}\gg k_{-\mathrm{en}(-\mathrm{el})}$) corresponding to a plateau value can be obtained from

$$k^{\mathrm{pl}}_{\mathrm{q}}=\frac{sk_{\mathrm{d}}k^0_{\mathrm{en(el)}}}{k_{\mathrm{en(el)}}+k_{-\mathrm{d}}} \tag{11}$$

The free energy of activation for energy- and electron-transfer processes ($\Delta G^{\neq}_{\mathrm{en}}$ and $\Delta G^{\neq}_{\mathrm{el}}$) can be related to the free-energy changes ΔG_{en} and ΔG_{el} by two types of relationship: "asymptotic" forms such as Agmon–Levine [28]

$$\Delta G^{\neq}_{\mathrm{en(el)}}=\Delta G_{\mathrm{en(el)}}+\frac{\Delta G^{\neq}_{\mathrm{en(el)}}(0)}{\ln 2}\ln\left[1+\exp\left(\frac{\Delta G_{\mathrm{en(el)}}\ln 2}{\Delta G^{\neq}_{\mathrm{en(el)}}(0)}\right)\right] \tag{12}$$

and the theoretical "quadratic" form of the classical Marcus theory [29,30]

$$\Delta G^{\neq}_{\mathrm{el}}=\frac{(\Delta G_{\mathrm{el}}+\lambda)^2}{4\lambda} \tag{13}$$

where λ is the reorganization energy. These parameters can be related by setting $\Delta G_{\mathrm{el}}=0$ in Eq. (13) to give

$$\Delta G^{\neq}_{\mathrm{el}}(0)=\frac{\lambda}{4} \tag{14}$$

If the quenching is described as a combination of energy and electron transfer, an analogous treatment leads to the following equation:

$$k_{\mathrm{q}}=sk_{\mathrm{d}}\left[1+\left(\frac{1}{\frac{k_{-\mathrm{d}}}{k^0_{\mathrm{en}}}\exp\left(\frac{\Delta G^{\neq}_{\mathrm{en}}}{RT}\right)+\exp\left(\frac{\Delta G_{\mathrm{en}}}{RT}\right)}+\frac{1}{\frac{k_{-\mathrm{d}}}{k^0_{\mathrm{el}}}\exp\left(\frac{\Delta G^{\neq}_{\mathrm{el}}}{RT}\right)+\frac{k_{-\mathrm{d}}}{k_{\mathrm{bt}}}\exp\left(\frac{\Delta G_{\mathrm{el}}}{RT}\right)}\right)^{-1}\right]^{-1} \tag{15}$$

The intrinsic barriers, $\Delta G^{\neq}_{\mathrm{en(el)}}(0)$, and transmission coefficients, $\kappa_{\mathrm{en(el)}}$, can be evaluated using Eq. (7) for energy-transfer quenching, Eq. (8) for electron-transfer quenching, or Eq. (15) for competitive energy and electron transfer, along with

Eqs. (5), (6), (12) and (13). This treatment requires the assumption that for a particular quencher, the initially excited molecules can be treated as a homologous series with constant $\Delta G^{\neq}_{\mathrm{en(el)}}(0)$ and $\kappa_{\mathrm{en(el)}}$ values. It also requires that all other parameters such as k_{d}, $k_{-\mathrm{d}}$, and k_{bt} are known. The appropriate diffusion rate constants k_{d} and the rate constants of dissociation of the precursor complex $k_{-\mathrm{d}}$ were estimated from the Debye and Eigen equations [31,32] as $k_{\mathrm{d}} = 1.9 \times 10^{10}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ and $k_{-\mathrm{d}} = 2.2 \times 10^{10}\ \mathrm{s}^{-1}$ [10,13] for acetonitrile at room temperature. Similar calculations for benzene solutions gave $k_{\mathrm{d}} = 1.0 \times 10^{10}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ and $k_{-\mathrm{d}} = 1.2 \times 10^{10}\ \mathrm{s}^{-1}$ [14–16]. Since the optimization (described below) was shown not to be sensitive to reasonable values of the rate constants for back-electron transfer ($k_{\mathrm{bt}} > 10^{8}\ \mathrm{s}^{-1}$), $k_{\mathrm{bt}} = k_{-\mathrm{d}}$ was used in the final calculations [13,14,16].

The formalism discussed above can be applied to obtain the details of quenching events by indirect means even when energy-transfer or electron-transfer intermediates are not observed. The first step in the method involves the determination of the quenching rate constants for a homologous series of organic triplet states by a particular ML_n complex. The rate constants were measured either by laser flash photolysis (by monitoring the time-resolved triplet–triplet absorbance at a fixed wavelength for various quencher concentrations) or by phosphorescence quenching (or photochemical reactions) by the ML_n complex. The next step was the evaluation of transmission coefficients and intrinsic barriers for energy and electron transfer using nonlinear least squares fits to the $\log k_{\mathrm{q}}$ vs. $\Delta G_{\mathrm{en(el)}}$ plots applying the appropriate equations (for energy transfer, electron transfer, or both as competitive processes) to the experimental k_{q} values.

3. Quenching of triplet states of organic compounds by 1,3-diketonates of lanthanides in solution

Because of their absorption and luminescence properties, lanthanide ions and their chelates are very good model compounds for studying energy-transfer processes. Therefore, the quenching of excited states of organic molecules by lanthanide ions and complexes in solution has been the subject of numerous investigations over the years. This work has been reviewed in part [9,33]. In this section a recent study of the quenching of organic triplet states by lanthanide 1,3-diketonates in solution will be summarized. The observation of characteristic, line-like sensitized emissions from Ln(III) in solution at room temperature can provide direct evidence for an energy-transfer mechanism of quenching. In addition, the correlation between $\log k_{\mathrm{q}}$ and ΔG_{en} for a series of organic energy donors and a particular LnL_3 complex as a quencher can lead to a quantitative description of the energy transfer to the ligand-localized triplet states and/or to the excited ff states of Ln(III) 1,3-diketonates. This can be done with the indirect method of studying quenching processes described in Section 2.

Direct evidence for the participation of an energy-transfer process in the quenching of benzophenone triplet states by $\mathrm{Ln(acac)}_3$ was obtained from steady-state and time-resolved emission studies. It was shown in the steady-state measurements that benzophenone phosphorescence can be quenched by Sm(III), Eu(III), Gd(III), Tb(III), and Dy(III) acetylacetonates in benzene and acetonitrile solutions at room temperature. In addition, sensitized emission was observed from Eu(III) and Tb(III) complexes [34]. The lack of sensitized emission from the other lanthanide quenchers was rationalized by citing their low intrinsic quantum yields of emission. In the case of Gd(acac)$_3$, its lowest radiative ff* level was higher than its ligand-localized triplet state (see Fig. 3); thus, no sensitized emission was expected. The time-resolved experiments with a Tb(III) quencher also clearly indicated the formation of a quencher excited state, Q*, after the termination of the laser pulse (Fig. 4) [10]. The correspondence between the rate constant of triplet decay with the rate constant for the rise of the Tb(III) emission is direct proof for the participation of an energy-transfer quenching ($k_{decay} = (2.2 \pm 0.1) \times 10^5$ s^{-1} and $k_{rise} = (2.7 \pm 0.6) \times 10^5$ s^{-1}).

The rate constants for quenching of the benzophenone triplet state by Ln(acac)$_3$ and lanthanide ions in acetonitrile are summarized in Table 1. The table includes values obtained both from the steady-state measurements [34] (quenching of benzophenone phosphorescence and sensitized emission of Ln(III)) and from the flash photolysis study [10] (decay of triplet–triplet absorption). From an examination of the data in Table 1, several observations relevant to an understanding of the quenching processes can be made:

(1) The benzophenone triplet state is quenched by a series of Ln(acac)$_3$ complexes

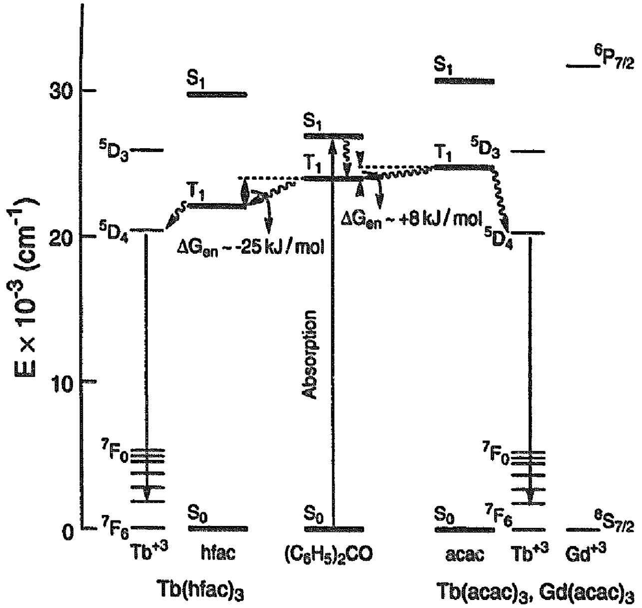


Fig. 3. Energy-level diagram for the lowest excited states of benzophenone, Tb(acac)$_3$, Gd(acac)$_3$, and Tb(hfac)$_3$ (from [34]).

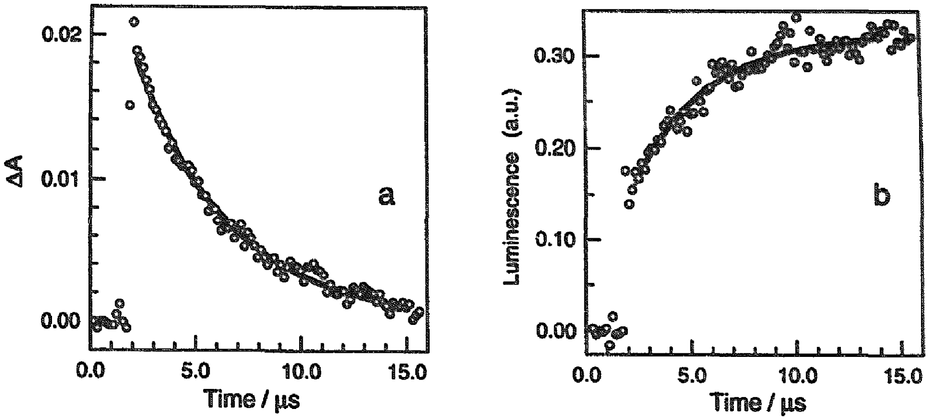


Fig. 4. (a) Decay of the triplet–triplet absorption of benzophenone monitored at 530 nm. (b) Rise of the sensitized emission of Tb(III) at 550 nm. Acetonitrile solution of 1 mM benzophenone and 0.19 mM $Tb(acac)_3$ (from [10]).

Table 1
Quenching of benzophenone triplet state by lanthanide acetylacetonates in acetonitrile

Quencher	$k_q \times 10^{-9}/M^{-1}\ s^{-1}$	
	From quenching of benzophenone phosphorescence[a]	From sensitized emission of Ln(III)[b]
$Sm(acac)_3$	0.94	–
$Eu(acac)_3$	0.88	0.7
$Gd(acac)_3$	1.0 (0.86)[c]	–
$Tb(acac)_3$	0.92[c]	0.7
$Dy(acac)_3$	0.95	–
$Mg(acac)_2$	1.1	–
Eu^{+3}	0.18	–
Tb^{+3}	0.04	–

[a] From [34], taking $\tau_p = 18$ µs; estimated uncertainties ±10%.
[b] From [34], taking $\tau_p = 18$ µs; estimated uncertainties ±30%.
[c] From [10]; value for $Gd(acac)_3$ was misprinted in [10].

(where Ln = Sm, Eu, Gd, Tb, or Dy) with essentially the same rate constant, $k_q \approx 9 \times 10^8\ M^{-1}\ s^{-1}$, for all complexes studied.

(2) k_q values for quenching by Eu^{+3} and Tb^{+3} ions are at least five times less than the k_q values associated with the corresponding $Ln(acac)_3$ complexes.

(3) Similar k_q values (within experimental error) are obtained from the quenching and sensitization measurements.

These observations point to the ligand-localized triplet state of the quencher as being the active state in the energy-transfer events. This conclusion is supported by comparing the k_q values in Table 1 with relevant energy gaps between the benzophenone triplet and the triplet states of the acetylacetonate (acac) and hexafluoroacetylacetonate (hfac) ligands of the quenchers (see Fig. 3 and [34]).

In order to get more detailed information on the events involving the quenching of the triplet state of organic compounds by 1,3-diketonates of lanthanides in solution, the indirect method discussed in Section 2 was applied. The indirect method consists of analyzing correlations of the k_q values for quenching of a series of organic triplet states by a given LnL_3 complex as a function of the standard free-energy change for energy transfer. As part of the procedure described in Section 2, the rate constants for quenching of nine different organic compounds by $Tb(acac)_3$, $Gd(acac)_3$, and for comparison, $Mg(acac)_2$ and $Mg(hfac)_2$, were determined by laser flash photolysis in acetonitrile solutions (see Table 2).

The dependence of k_q on the energy, E_T, of the triplet state of the energy donors being quenched, is presented in Fig. 5. (According to Eq. (5), for a particular quencher, any functional dependence of k_q on E_T will be the same as that of k_q on ΔG_{en}, up to a linear displacement in the independent variable.) The two curves represent archetypical energy transfer behavior in that the rapid changes in their slope correspond to electronic transitions in the quenchers. The observed plots allowed a distinction to be made between the energy transfer to the ligand-localized triplet state of the acac ligand (dotted curve) and the energy transfer to the excited ff states of $Tb(acac)_3$ (broken curve). Transmission coefficients κ_{en} for these energy transfer processes can be computed from the plateau values in Fig. 5 with the application of Eqs. (10) and (11). κ_{en} for transfer to the excited ff state of $Tb(acac)_3$ was computed to be 2.4×10^{-6}; while that for transfer to its acac triplet state was estimated to be approximately 10^{-3} (see Table 3 for these and other values of κ_{en}). The magnitude of κ_{en} obtained for $Tb(acac)_3$ indicates a much stronger

Table 2
Rate constants for quenching of the triplet states of organic molecules by metal complexes in deoxygenated acetonitrile solution at room temperature (from [10])

No.	Molecule	$k_q \times 10^{-9}/M^{-1}\,s^{-1}$ [a]			
		$Tb(acac)_3$	$Gd(acac)_3$	$Mg(acac)_2$	$Mg(hfac)_2$
1	Xanthone	7.6	7.4	5.5	5.4
2	4,4′-Dimethoxybenzophenone	0.47	0.44	0.44	3.2
3	Benzophenone	0.92	0.86[b]	1.1	3.3
4	4-Trifluoromethylbenzophenone	2.2	2.2	2.7	3.2
5	Triphenylene	0.01[c]	≤0.002	≤0.02	3.1
6	Phenanthrene	0.002[c]	≤0.001	–	0.015
7	Naphthalene[d]	0.003[c]	≤0.001	–	0.0008[c]
8	Chrysene	0.001[c]	–	–	–
9	Dibenz[*a*,*h*]anthracene	≤0.0005	–	–	–

[a] Estimated uncertainties, ±10% or less.
[b] This value was misprinted in [10].
[c] Estimated uncertainties, ±50% or less.
[d] Sensitized with benzophenone.

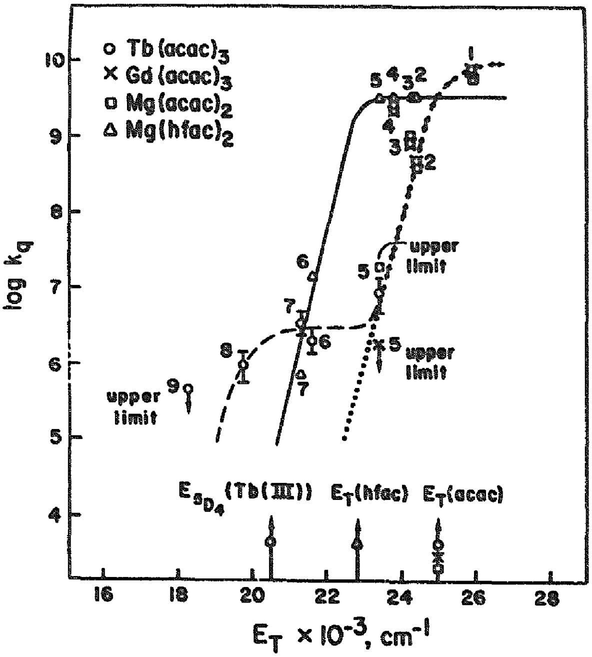


Fig. 5. Energy transfer: dependence of the quenching rate constant, k_q, on the energy, E_T, of the triplet states (see Table 2 for definition of the numbers) being quenched by Tb(acac)$_3$, Gd(acac)$_3$, Mg(acac)$_2$, and Mg(hfac)$_2$ in acetonitrile. The arrows indicate electronic transitions to the lowest excited states of the quenchers used (from [10]).

nonadiabatic character of the energy transfer to transition metal 1,3-diketonates when the metal-centered f orbitals are involved than when ligand orbitals are involved. Large experimental errors in the determination of k_q values for the lanthanides did not allow an evaluation of the intrinsic barriers for these processes to be made with any confidence.

For contrast with complexes containing metals having filled f orbitals, magnesium complexes were also used as triplet quenchers. A nonlinear least-squares fitting procedure based on Eq. (7) (energy-transfer quenching) allowed an estimation to be made of the intrinsic barrier for the energy transfer to the ligand-localized triplet state of Mg(hfac)$_2$. The estimate was approximately 140 cm^{-1} (Table 3) using the asymptotic Agmon–Levine free-energy relationship (Eq. (12)) and approximately 290 cm^{-1} using the Marcus quadratic free-energy relationship (Eq. (13)) [10]. The small value of $\Delta G^{\neq}_{en}(0)$ indicates that an undistorted state of Q* is produced in the energy transfer.

As indicated in Fig. 5, the benzophenones (compounds **2**, **3**, and **4**) deviated in a systematic way from the archetypical energy-transfer behavior exhibited by the other triplets. The decrease in the k_q values of the benzophenone derivatives with an increase in the algebraic value of $-(E_T+E_{red})$ was taken as a strong evidence for the participation of an additional quenching process. Since $-(E_T+E_{red})$ is a driving

Table 3
Transmission coefficients, κ_{en}, and intrinsic barriers, $\Delta G^{\ddagger}_{en}(0)$, for energy transfer to 1,3-diketonate metal chelates as determined from the best fit to the experimental results using the Agmon–Levine free-energy relationship

Quencher	Solvent	κ_{en}	$\Delta G^{\ddagger}_{en}(0)$/cm^{-1}	Active Q* level
Cu(acac)$_2$[a]	Benzene	4.3×10^{-3}	800	dd state
Cu(hfac)$_2$[b]	CH_3CN	$\approx6\times10^{-3}$	150	$^3L^*$
Ni(acac)$_2$[b]	CH_3CN	8.0×10^{-5}	485	dd state
Ni(hfac)$_2$[b]	CH_3CN	$\approx1.7\times10^{-5}$	–	dd state
		8.8×10^{-5}	125	$^3L^*$
Tb(acac)$_3$[c]	CH_3CN	2.4×10^{-6}	–	ff state
		$\approx10^{-3}$	–	$^3L^*$
Gd(acac)$_3$[c]	CH_3CN	$\approx10^{-3}$	–	$^3L^*$
Mg(acac)$_2$[c]	CH_3CN	$\approx10^{-3}$	–	$^3L^*$
Mg(hfac)$_2$[c]	CH_3CN	7.2×10^{-4}	140	$^3L^*$
Cr(acac)$_3$[d]	Benzene	1.6×10^{-3}	–	dd (^2E_g,$^2T_{2g}$)
		2.6×10^{-3}	2000	dd ($^4T_{2g}$)
Cr(hfac)$_3$[d]	Benzene	1.3×10^{-3}	–	dd (^2E_g,$^2T_{1g}$)
		3.3×10^{-3}	2200	dd ($^4T_{2g}$)
Fe(acac)$_3$[d]	Benzene	2.4×10^{-4}	–	dd ($^4T_{1g}$)
		1.6×10^{-4}	–	dd ($^4T_{2g}$)
		1.5×10^{-3}	320	CT state (^{6}CT)

[a] From [16]. [b] From [13]. [c] From [10]. [d] From [11,12].

force for electron transfer (see Eq. (6)), electron transfer from the acac ligand to the benzophenone triplet state is the likely process. The extra reaction occurred in the systems consisting of triplet states of benzophenone derivatives with Ln(acac)$_3$ and Mg(acac)$_2$ as quenchers. This type of electron transfer was suggested to be a primary photochemical reaction in the aromatic ketone-sensitized photoreduction of Cu(II) and Ni(II) acetylacetonates in hydrogen-donating solvents [2,17–22] (see below).

4. Quenching of triplet states of organic compounds by 1,3-diketonates of nickel(II) and copper(II) in solution

In contrast to the lanthanide complexes, the copper(II) and nickel(II) 1,3-diketonates do not emit in solution. In the quenching experiments, no transient absorption spectra of their excited states could be detected, and no short-lived transients were found that could be ascribed to electron-transfer intermediates, either of the electron donors or acceptors. Therefore, no direct evidence for energy- or electron-transfer quenching was established experimentally. Indirect evidence concerning the nature of the quenching of organic triplets by 1,3-diketonates of Cu(II) and Ni(II) turned out to be revealing. The method again involved consideration of the dependence of the quenching rate constants, k_q, for a series of organic compounds, on the standard free-energy changes for energy-transfer and/or electron-transfer processes, ΔG_{en} or ΔG_{el} according to Eqs. (7), (8) and (15). In this section some recent studies on the triplet quenching of organic compounds by Ni(II) and Cu(II) 1,3-diketonates are reviewed.

Fifteen organic compounds with the triplet-state energies varying from 8000 to 25 900 cm^{-1} were used as precursors for triplets which were quenched by $Cu(acac)_2$, $Cu(hfac)_2$, $Ni(acac)_2$, and $Ni(hfac)_2$ in acetonitrile [13]. The quenching rate constants, k_q, were measured by monitoring the triplet–triplet absorption decays of the donor at fixed wavelengths for various quencher concentrations using the nanosecond laser flash photolysis technique. The measured k_q values for Cu(II) and Ni(II) 1,3-diketonates are summarized in Table 4.

The same quantitative evaluation of the quenching rate constants that was used for lanthanide 1,3-diketonates was done on the quenching of triplet states of organic compounds by $Ni(acac)_2$ and $Ni(hfac)_2$ in acetonitrile. If quenching by Ni(II) complexes were due only to energy transfer, one would expect a correlation similar to that found for $Tb(acac)_3$, where $\log k_q$ varied sharply as the energy of the triplet state being quenched matched the quencher's electronic levels. Fig. 6 shows the results obtained for 1,3-diketonates of Ni(II) and indicates quite a good correlation of $\log k_q$ vs. E_T for both $Ni(acac)_2$ and $Ni(hfac)_2$. As discussed in [13], electron transfer from these triplet states to the Ni(II) complexes can be neglected based on free-energy considerations (calculated using Eq. (6) $\Delta G_{el} > +0.1$ eV for $Ni(acac)_2$

Table 4
Rate constants for quenching of the triplet states of organic molecules by transition-metal complexes in deoxygenated acetonitrile solution at room temperature (from [10])

No.	Triplet state	$k_q \times 10^{-9}$/M^{-1} s^{-1c}			
		$Cu(acac)_2$	$Cu(hfac)_2$	$Ni(acac)_2$	$Ni(hfac)_2$
1	Xanthone	8.5	6.9	5.9	4.9
2	4,4′-Dimethoxybenzophenone	4.6	5.0	1.5	3.2
3	Benzophenone	5.3	5.5	3.0	3.6
4	4-Trifluoromethylbenzophenone	6.7	4.2	4.2	3.5
5	Triphenylene	3.0	4.3	0.46	4.7
6	Phenanthrene	3.3	4.1	0.18	2.3
7	Naphthalene[a]	2.5	2.7	0.15	1.3
8	Chrysene	2.9	1.9	0.14	0.036
9	Dibenz[*a*,*h*]anthracene	2.9	1.7	0.13	0.02[d]
10	Pyrene	1.9	1.2	0.13	0.029
11	Anthracene	1.25	0.80	0.15	0.014
12	Perylene[b]	0.55	0.54	0.12	≤0.006
13	Tetracene[b]	0.027	0.38	0.081	–
14	Rubrene[b]	≤0.006	0.035	0.013	–
15	Pentacene	0.013	–	≤0.001	–

[a] Sensitized with benzophenone.
[b] Sensitized with anthracene.
[c] Estimated uncertainties, ±10%.
[d] Estimated uncertainties, ±50%.

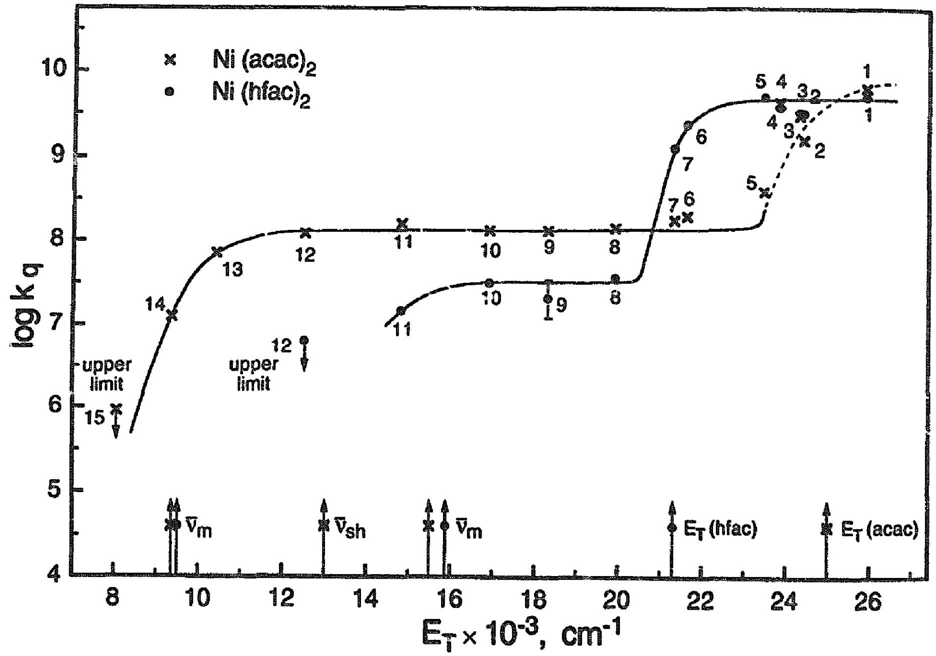


Fig. 6. Energy transfer: dependence of the quenching rate constant, k_q, on the energy, E_T, of the triplet states (see Table 4 for definition of the numbers) being quenched by Ni(acac)$_2$ and Ni(hfac)$_2$ in acetonitrile. The arrows indicate the electronic transitions to the lowest excited states of the Ni(II) chelates (from [13]).

and $\Delta G_{el} > -0.04$ eV for Ni(hfac)$_2$ for all triplets studied). In the case of Ni(acac)$_2$ Fig. 6 shows a log k_q vs. E_T plot that has a linear region for sufficiently endoergonic reactions, followed by an intermediate region (for compounds with triplet energies close to the energy of the lowest excited state of Ni(acac)$_2$), and finally followed by a plateau for k_q when energy transfer is very exoergonic. In contrast to the results for Cr(III) and Fe(III) 1,3-diketonates [4–6,11,12], a stepwise increase of log k_q for E_T values close to the energies of the next higher metal-centered excited states of Ni(acac)$_2$ was not observed. In the case of Ni(hfac)$_2$, because of experimental limitations, $k_q < 10^7$ M^{-1} s^{-1}, the first plateau was observed only for a higher excited metal-centered state ($\bar{\nu} = 15\,800$ cm^{-1}). The first plateau was followed by a step in the k_q values close to the energy of the ligand-localized triplet states for both Ni(acac)$_2$ and Ni(hfac)$_2$. Since this behavior indicated only one active state in the quencher (in the neighborhood of each of these steps), a two-parameter fit according to Eq. (7) was used to obtain appropriate transmission coefficients κ_{en} and intrinsic barriers $\Delta G^{\neq}_{en}(0)$. The results are summarized in Table 3.

The lack of some steps in the log k_q vs. E_T plots for the onset of all of the excited states of the Ni(II) compounds (contrary to the Cr(III) and Fe(III) 1,3-diketonates [4–6,11,12]) may be due to the change in the values of spin-statistical factors for various excited states of Ni(II) complexes or due to orbital symmetry (for details see [13]). Thus, quenching by $Ni(acac)_2$ and $Ni(hfac)_2$ is adequately described by energy transfer to excited metal-centered states or to ligand-localized triplet states. However, similar to $Ln(acac)_3$ and $Mg(acac)_2$, in the case of $Ni(acac)_2$ and benzophenone triplet states, an additional quenching process, i.e. electron transfer from the acac ligand to the triplet state of the benzophenones, may occur. This can be seen in Fig. 6 where the benzophenone derivatives (compounds **2**, **3**, and **4**) deviate from the classical energy-transfer behavior which was followed by the other triplet states in this study.

Quenching of the triplet states of organic compounds by $Cu(hfac)_2$ in acetonitrile can be adequately described as a result of electron-transfer quenching (electron transfer from the triplet state to the Cu(II) complex). This conclusion was based on the quantitative evaluation of the quenching data (Table 3) using appropriate equations for energy transfer (Eq. (7)), electron transfer (Eq. (8)), and both as competitive processes (Eq. (15)). To avoid an additional energy-transfer process, i.e. energy transfer to the ligand-localized triplet state of $Cu(hfac)_2$, the fitting procedure was performed for compounds **7–14**. These compounds have energies of their triplet states below the energy of the $^3L^*$ state of $Cu(hfac)_2$, estimated to be 21 500 cm^{-1} (Fig. 7). The fitted values of κ_{el} and $\Delta G^{\neq}_{el}(0)$ were obtained from Eq. (8) (electron-transfer quenching) using the Agmon–Levine free-energy relationship (Eq. (12)) and the Marcus free energy relationship (Eq. (13)).

The resulting parameters were shown to be in the same range regardless of the free energy relationship used. The computed k_q values from the best-fit values of the electron-transfer parameters are displayed as a solid curve for the Agmon–Levine free-energy relationship and as a dashed curve for the Marcus free-energy relationship (Fig. 7). Thus, the quantitative evaluation of the experimental data using quadratic and asymptotic relationships led to similar values of the intrinsic barriers and transmission coefficients. Fig. 7 also shows the results of the application of the quantum-mechanical theory [35] and the semiclassical electron-transfer theory (with the Tachiya–Murata diffusion kinetics extension [36]). Details of these calculations are presented in [13]. Considering the diversity of the theoretical models, the physical parameters obtained from the fittings are quite consistent with each other and with the notion that the electron transfer in these systems is nonadiabatic in nature.

In order to incorporate the data points associated with triphenylene (**5**) and phenanthrene (**6**), energy transfer to the hfac ligand triplet was considered. The experimental k_q values were analyzed from Eq. (15) as resulting from competitive energy- (to the ligand triplet) and electron-transfer processes. For this analysis, compounds **5–14** were included. $\Delta G^{\neq}_{en(el)}(0)$ and $\kappa_{en(el)}$ were the four fitting parameters. All the fixed parameters (diffusion-controlled rate constants for acetonitrile, transition energies, and redox potentials) were kept the same as for the two-parameter fits (see above) of the $Cu(hfac)_2$ data. The calculated k_q values based on these four fitting parameters are shown in Fig. 8 as open circles. The two electron-transfer parameters, $\Delta G^{\neq}_{el}(0)$ and κ_{el}, from the four-parameter fit using data from compounds **5–14** were similar to the two analogous electron-transfer parameters from the two-parameter fit where data for compounds **7–14** were used. This shows that quenching

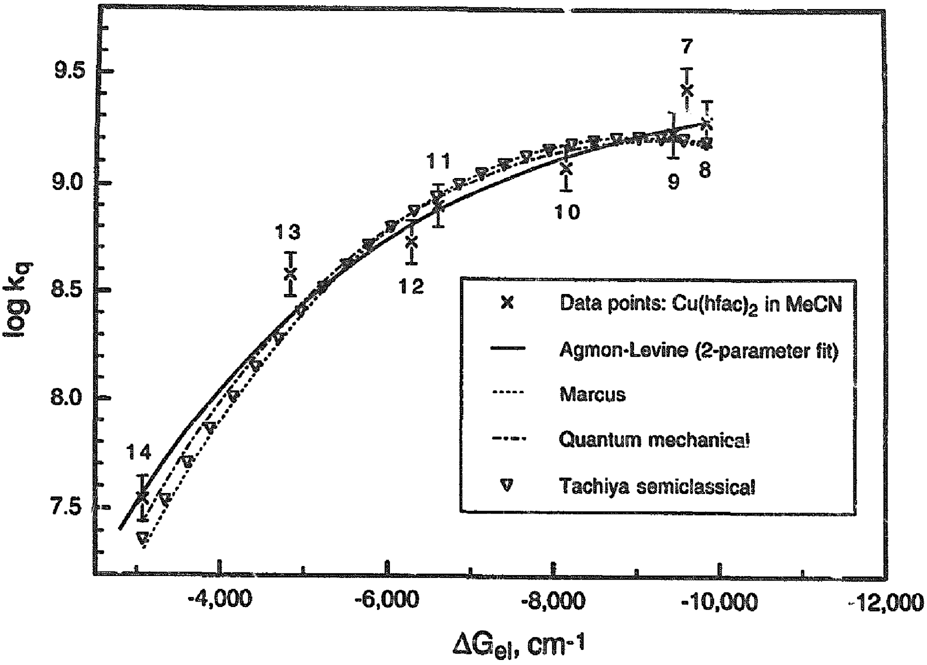


Fig. 7. Electron transfer: dependence of the triplet quenching rate constant, k_q, on the free-energy change, ΔG_{el}, for electron transfer to $Cu(hfac)_2$ in acetonitrile. Numbers corresponding to the triplet states are given in Table 4. The curves are the results of applying various theories of electron transfer and diffusion kinetics to the experimental data. These fittings are described in detail in [13].

data for compounds **7–14** are described by electron-transfer quenching without competition from energy transfer to the ligand-localized triplet, but quenching of the higher-energy triplets (**5** and **6**) required the consideration of energy transfer to the ligand-localized state of the quencher in order to be described adequately.

A similar treatment was performed for the quenching of aromatic hydrocarbon triplets (compounds **5–14**) by $Cu(hfac)_2$ in benzene and by $Cu(acac)_2$ in benzene and acetonitrile [13,16]. Many of these fitting results are summarized in Tables 3 and 5 in addition to the results for Cr(III) and Fe(III) acetylacetonates and hexafluoroacetylacetonates measured by Wilkinson and co-workers [4–6, 11,12,14,15].

As shown in Table 3, the values of transmission coefficients for energy transfer to dd states of transition-metal 1,3-diketonates of Cu(II), Ni(III), Cr(III), and Fe(III) are in the range 10^{-3}–10^{-5} depending on the metal atom used and the type of active excited state in the quencher. The energy transfer to the ligand-localized triplet states is described by κ_{en}s in the range 10^{-3}–10^{-4}, and κ_{en}s for energy transfer to the excited ff states of lanthanide complexes are in the order of 10^{-6}. This indicates a much stronger nonadiabatic character of the energy transfer to the transition-metal complexes when the metal-centered f orbitals are involved compared to when d

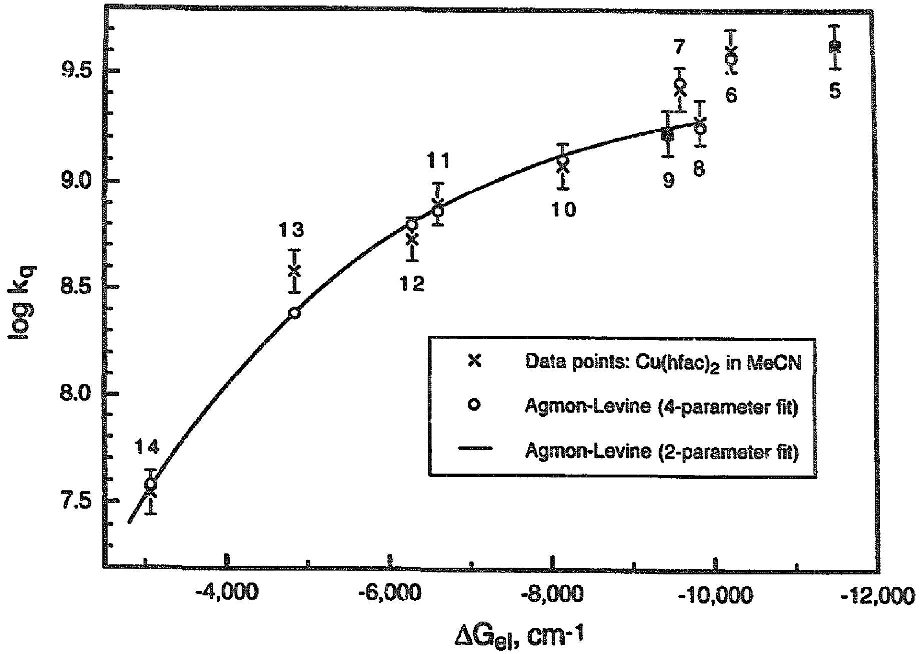


Fig. 8. Competitive electron and energy transfer: same data as in Fig. 7 for quencher $Cu(hfac)_2$ in acetonitrile. The comparison is made between fitting data for quenching of triplet states 7–14 (only electron-transfer quenching) with fitting data for triplet states 5–14 (competitive energy and electron transfer) (from [13]).

Table 5
Transmission coefficients, κ_{el}, and intrinsic barriers, $\Delta G^{\ddagger}_{el}(0)$, for electron transfer from the triplet state of organic compounds to 1,3-diketonate metal chelates as determined from the best fit to the experimental results using the Agmon–Levine free-energy relationship

Quencher	Solvent	κ_{el}	$\Delta G^{\ddagger}_{el}(0)/cm^{-1}$
$Cu(acac)_2$[a]	CH_3CN	3.3×10^{-3}	860
$Cu(hfac)_2$[a]	CH_3CN	3.0×10^{-3}	2200
	Benzene	5.8×10^{-3}	1500
$Cr(hfac)_3$[b]	Benzene	2.4×10^{-3}	1300
$Fe(hfac)_3$[b]	Benzene	2.1×10^{-3}	2000

[a] From [13].
[b] From [11,12].

orbitals or ligand orbitals are involved. The values of intrinsic barriers in Table 3 indicate that an undistorted ligand-localized excited triplet state and distorted excited dd states of ML_n complexes are produced in the energy-transfer processes studied.

As presented in Table 5, the transmission coefficients for electron transfer are in the range of 10^{-3} and are similar for all the complexes considered. This illustrates the nonadiabatic character of the electron-transfer process. The role of solvent in the intrinsic barrier for electron transfer was discussed for the $Cu(hfac)_2$ complex in [13]. Changing the solvent from benzene to acetonitrile leads to an increase in the value of the intrinsic barrier (Table 5). This can be accounted for by the larger solvent reorganization energy in acetonitrile. However, $\Delta G^{\ne}_{el}(0)$ obtained from the fitting procedure for $Cu(acac)_2$ in acetonitrile (Table 5) is significantly smaller than expected. It should be one quarter of the solvent reorganization energy (Eq. (14)) which was calculated within the framework of the dielectric-continuum model for spherical molecules [13]. This discrepancy could be due to either the inadequacy of the solvent-continuum model for calculating the reorganization energy or to an unknown competing quenching mechanism [13].

In the case of the quenching of triplet states of benzophenone derivatives by Ln(III), Mg(II), Ni(II) and Cu(II) acetylacetonates (Tables 2 and 4, Figs. 5 and 6), an additional quenching process, that is electron transfer from the acetylacetonate ligand to the benzophenone triplet states, was suggested. This suggestion was based on the decrease in the k_q values of the benzophenone derivatives (compounds 2–4) with an increase in the algebraic value of $-(E_T+E_{red})$ (the more negative the value, the more negative the standard free energy for electron transfer, Eq. (6)). This type of electron-transfer quenching was also suggested by Chow and co-workers [2,17–22] to be a primary photochemical reaction in the benzophenone-sensitized photoreduction of $Cu(acac)_2$ and $Ni(acac)_2$ in hydrogen-donating solvents.

$$\mathrm{Ar_2C{=}O^* + Cu(acac)_2 \xrightarrow{k_q} \left[Ar_2C{=}O^{\bullet -} \cdots Cu(acac)_2^{\bullet +}\right]} \tag{16}$$

$$\mathrm{\left[Ar_2C{=}O^{\bullet -} \cdots Cu(acac)_2^{\bullet +}\right] + SH \xrightarrow{k_{17}} Ar_2C{=}O + Cu(acac) + acacH + S^{\bullet}} \tag{17}$$

$$\mathrm{\left[Ar_2C{=}O^{\bullet -} \cdots Cu(acac)_2^{\bullet +}\right] \xrightarrow{k_{18}} Ar_2C{=}O + Cu(acac)_2} \tag{18}$$

Electron transfer as a primary photochemical process proposed in Eq. (16) was supported by the correlation of $\log k_q$ vs. $(-E_T-E_{red})$ (see Eq. (6)) for a series of benzophenone derivatives containing electron-donating or electron-withdrawing groups and with $Cu(acac)_2$ as the quencher in methanol. The k_q values were determined by quenching of benzophenone phosphorescence and by the measurements of quantum yields of sensitized photoreduction of $Cu(acac)_2$ for various quencher concentrations [3,22]. The resulting plot (Fig. 9) gives strong evidence in favor of electron transfer from the acac ligand to the benzophenone triplet state. The lack of correlation between $\log k_q$ and E_T (energies of benzophenone triplet states are similar for all benzophenone derivatives used [22]) indicates that energy transfer is not responsible for quenching.

In summary, quenching of excited states of organic compounds by 1,3-diketonate transition-metal chelates (ML_n) in solution may occur by a competition between

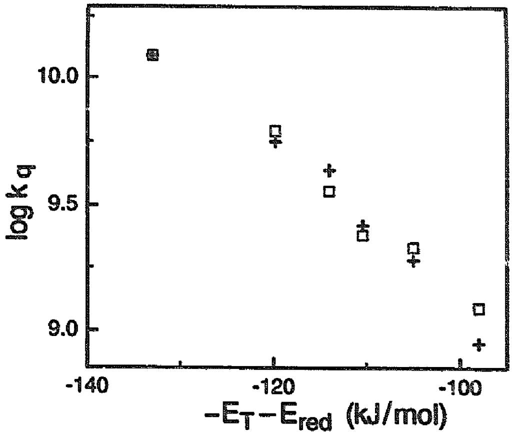


Fig. 9. Dependence of the quenching rate constant, k_q, on $-(E_T+E_{red})$ for quenching of substituted benzophenone triplet states by $Cu(acac)_2$ in methanol (from [22]).

various quenching processes such as energy transfer to different excited states of ML_n complexes (metal-centered dd and ff states, ligand-localized states, CT states) and as electron transfer to or from the quencher molecule.

Acknowledgements

This work was supported by the Office of Basic Energy Sciences of the US Department of Energy and is Document No. NDRL-3871.

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