Sensitization and Quenching Processes of Alkylcobalt(III) Compounds

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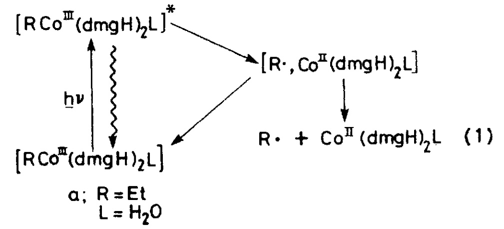
Ethyl(aquo)cobaloxime is found to be a potent quencher of a wide variety of excited states. Laser flash photolysis studies show that triplet states of organic molecules with $E_T > 170$ kJ mol^{-1} are quenched at rates exceeding 10^9 dm^3 mol^{-1} s^{-1}, while those of rubrene and β-carotene, with $E_T < 110$ kJ mol^{-1}, are not effectively deactivated. A variety of excited states of inorganic molecules are also quenched at rates exceeding 10^9 dm^3 mol^{-1} s^{-1} by ethyl(aquo)cobaloxime: the insensitivity of the quenching rate to the reduction potentials of the excited states concerned (differing by 1.8 V) indicates a mechanism of energy (rather than electron) transfer. Analogous kinetic studies have been carried out, by way of comparison, on tris(acetylacetonato)cobalt(III) and a few studies on methylcobalamin. A number of the quenchers examined have been shown to sensitize the photodecomposition of ethyl(aquo)cobaloxime, indicating the mechanism of energy transfer to be one of transfer to the photodissociative state of the alkylcobalt(III) compound: this is dissociated very efficiently by donors with energies as low as 170 kJ mol^{-1} (14 210 cm^{-1} or 704 nm) compared with the energy of its longest wavelength transition of 262 kJ mol^{-1}.

The photochemistry of alkylcobalt(III) compounds has attracted intense interest over the last decade,[1-7] principally because the primary photochemical homolytic cleavage exemplified in equation (1) for an alkylcobaloxime is regarded by several groups as a model for the biochemical transformations induced by the group of enzymes based on vitamin B_{12}. The proposed primary photohomolysis, equation (1), is now widely accepted as the main photoprocess, for both alkylcobaloximes and alkylcobalamins especially as a result of the spin-trapping of R· in solution,[3] the detection by e.s.r. of an R·–Co^{II} interaction in the solid state following photolysis,[4] and the typical free-radical chemistry of the R group following irradiation,[2] *e.g.* the cyclisation of R = cyclopentylmethyl to products derived from n-hexenyl radical.[5] The partial fast thermal reversal of equation (1) has also been noted following flash photolysis.[1c,6]

The ready photodecomposition of alkylcobaloximes with light of rather low energy,[7] *e.g.* φ *ca.* 0.17 for methyl(aquo)cobaloxime for λ(irr.) 439 nm (aqueous solution, pH 2),[7a] implies that these materials may be very potent quenchers of triplet excited states of organic molecules and excited states of inorganic complexes, and furthermore, that their decomposition may be sensitised by energy-transfer, as are those, for example, of hexammine and aquopentammine complexes of Co^{III} by organic triplet states,[8] and this topic forms the substance of this paper. To enable some comparison with another neutral complex of Co^{III}, we also investigated triplet quenching by tris(acetylacetonato)cobalt(III), denoted Co(acac)$_3$, for which photodecomposition quantum yields in the *visible* region are reported [9] to be *ca.* 10^{-3}. The quenching powers of Schiff bases and β-diketone complexes of other transition metal ions, especially Cr^{III}, towards organic triplet states have been a major topic of Wilkinson's group for some years,[10] while a brief report has appeared [11] of the quenching of the 'solar energy complex', [Ru(bipy)$_3$]$^{2+}$ (bipy = 2,2′-dipyridine), by a series of ketoenolates of Co^{III}.

We were also concerned to show that the homolytic fission of (1) could be induced by very low sensitization energies, *cf.* the recent demonstration that PhCoBAE [BAE = the dianion of *NN*′-ethylenebis(acetylacetoneimine)] undergoes homolysis on exposure to laser irradiation at 632.8 nm.[4a]



Experimental

Materials.—Ethyl(aquo)cobaloxime (1a) was prepared after Schrauzer [12a] and its purity checked by ^{1}H n.m.r.; in aqueous buffer at pH 5 it featured bands at 390 (ε 1.36×10^3 dm^3 mol^{-1} cm^{-1}) and 456 nm (1.24×10^3; *cf.* 1.38×10^3 in alcohol–water [12b]). Methylcobalamin was a gift from Dr. B. T. Golding. The organic sensitizers were purchased as AnalaR or scintillation grade materials where possible, otherwise purification was by recrystallisation. Water was refluxed over KMnO$_4$–OH$^-$ and doubly distilled and organic solvents were of spectroscopic grade except acetone, which was (as AnalaR grade material) submitted to prolonged refluxing over KMnO$_4$ before fractional distillation.

Laser Flash Photolysis.—This was performed with 40 ns pulses of 347 nm radiation as described before,[13] with the apparatus set up in either absorption or emission mode as required, and utilising a Hamamatsu red-sensitive photomultiplier (model R-666S). While the organic donors were monitored at maxima of their $T_1 - T_2$ absorption following excitation of their S_1 state, in the case of β-carotene it was necessary to sensitize the triplet state with 1-chloroanthracene as donor. Samples were deoxygenated by bubbling for 10—15 min with argon (B.O.C.; purity 99.999%). Temperatures were 21.5 ± 1.5 °C. Oscilloscope traces were analysed and rate constants derived with least-squares programs described previously.[13] Second-order quenching rate constants were obtained by normal procedures, and are typified in Figures 1 and 2. Fluorescence and phosphorescence data were obtained with a Perkin-Elmer model MPF-3 spectrofluorimeter equipped, when necessary, with a cryogenic device (*cf.* ref. 13) and a Hamamatsu R-666S red-sensitive photomultiplier tube.

Pulse Radiolysis.—This was carried out at the Cookridge Radiation Research Centre, Leeds University, using the systems of pulsed electron irradiation, sample preparation, and data analysis described previously.[14]

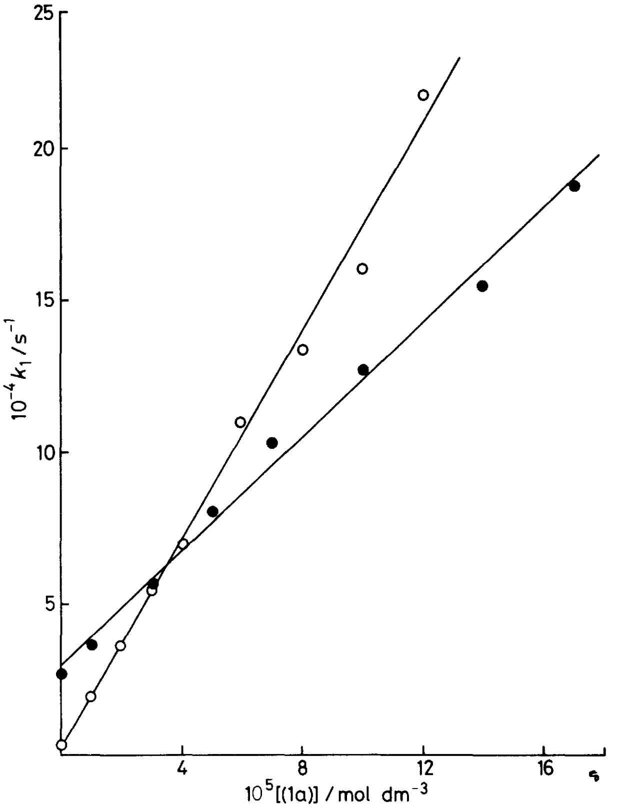


Figure 1. Dependence of first-order decay constants for excited states upon concentration of (1a). ○, Triplet state of 1-chloroanthracene (E_T 176.3 kJ mol^{-1}) monitored at $T - T$ absorption maximum 430 nm (MeOH solvent). ●, ^2E_g state of [Cr(phen)$_3$]$^{3+}$ (E 163.8 kJ mol^{-1}) monitored at emission maximum 730 nm (solvent, 0.01M aqueous HCl). (The straight lines refer to least-squares analysis of the data)

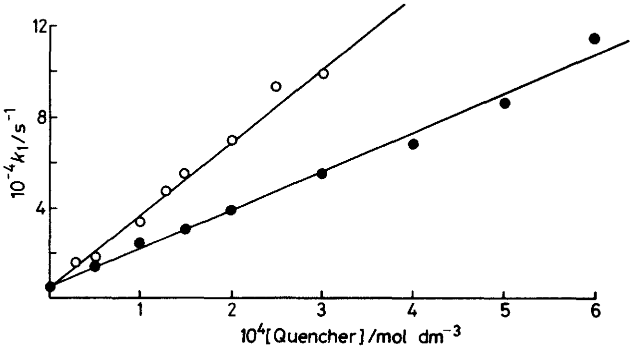


Figure 2. Dependence of the first-order decay constant of triplet 9,10-dichloroanthracene (E_T 169.2 kJ mol^{-1}) in dioxan solution upon the concentrations of (1a) (○) and Co(acac)$_3$ (●). Monitoring wavelength 420 nm. (The straight lines refer to least-squares analysis of the data)

Sensitization Experiments.—The irradiation source, optical bench, and procedure for actinometry have been described before.[7a] Approximately monochromatic light was produced by passage of the u.v. beam through Balzer metal interference filters. In general, concentrations of organic donor and (1a) were chosen such that a very high proportion, usually >98%, of the (filtered) light was absorbed by the donor. The photodecomposition of (1a) was monitored at either of its charge transfer transitions, *i.e.* 390 or 456 nm, depending on the absorption characteristics of the donor; indeed it was necessary to select donors which did not absorb strongly at one of these wavelengths, but did absorb strongly elsewhere. The quartz photolysis chamber measured 5 cm (depth) by 2.5 cm (diameter) and on to its sidearm (at 90°) was glass-blown a 1 cm quartz spectrophotometer cell, enabling absorbance and spectral measurements to be performed easily as photolysis proceeded. The sidearm terminated in a Teflon tap of 1 mm bore enabling the insertion of <1 mm diameter Teflon tubing for argon bubbling of solutions prior to photolysis.

Spectral Measurements.—^{1}H N.m.r. spectra were taken on a Perkin-Elmer model R-34 220 MHz spectrometer, while u.v.–visible spectra were measured on Perkin-Elmer 552 and Shimadzu 365 instruments. Single wavelength u.v. work was performed mostly on a Unicam SP 500 machine.

Results

Quenching of Organic Triplets States.—Laser flash photolysis of solutions of all the organic donors listed in Table 1(a) gave transients (in absorption) readily assigned from comparison with the literature to donor triplet states and in most cases with an absorbance at $\lambda_{max.}$ enabling quenching experiments to be performed, as typified in Figures 1 and 2. The low solubility of naphthacene presented problems, and its triplet decay approximated to second-order rather than first-order kinetics, even in the presence of quencher. Consequently, in the case of (1a), the initial rates method was employed to give a quenching rate of (2.56 ± 0.36) × 10^8 dm^3 mol^{-1} s^{-1}.

β-Carotene required the use of a triplet sensitizer[10] to produce its triplet state absorption, and here the kinetics of triplet formation were on a similar timescale to those of triplet decay, requiring the use of a series-first-order computer program[15] to factorise the two rate constants. For both (1a) and Co(acac)$_3$, the quenching rate constant was rather insensitive to the presence of quencher, with k_q estimated to be $\not> 10^7$ dm^3 mol^{-1} s^{-1} for (1a) and $\not> 2 \times 10^7$ dm^3 mol^{-1} s^{-1} for Co(acac)$_3$.

Rubrene triplet states were generated by pulse radiolysis of a benzene solution of rubrene (10^{-4} mol dm^{-3}) containing biphenyl (0.1 mol dm^{-3}) as energy transfer agent. This procedure gave an intensely absorbing transient with $\lambda_{max.}$ *ca.* 475 nm (Figure 3) decaying with τ 109 μs (Figure 3) [*cf.* literature figures of 125 (EtOH; 25 °C), [16a] 80—120 (MeCN),[16b] and 112 μs (benzene) [16c]]. The spectrum is in excellent agreement with that of Yildiz *et al.*[16c] obtained by a flash photolysis sensitization procedure. Addition of methanol (to 10%) was required to solubilise (1a) as quencher, but in this case the oscilloscope traces showed decay to an ultimate analysing light level indicating *enhanced* transmission following the pulse, suggesting fast sensitized decomposition of (1a) by rubrene triplets. Analysis of the initial parts of the decay indicated the quenching rate constant k_q to be $\not> 10^7$ dm^3 mol^{-1} s^{-1}. With Co(acac)$_3$ as quencher, the rubrene triplet decay at 475 nm was normal, *i.e.* with no enhanced transmission following the electron pulse, and only modest quenching was observed with k_q (3.60 ± 0.31) × 10^7 dm^3 mol^{-1} s^{-1}.

Organic donors with triplet energies exceeding *ca.* 170 kJ mol^{-1} are quenched very effectively by (1a), with $k_q > 10^9$ dm^3 mol^{-1} s^{-1}. The quenching rate appears to fall sharply with E_T values <170 kJ mol^{-1}, and the results which are summarised in Table 1(a) may be formulated as a Wilkinson plot (Figure 4). Co(acac)$_3$ also acts as an effective quencher for organic triplets (Table 2), but with generally lower rates k_q; again, a Wilkinson plot[10] can be constructed (Figure 5).

Table 1. Quenching of excited states by ethyl(aquo)cobaloxime

(a) Organic triplet states

Donor	Analysing wavelength (absorption) (nm)	Triplet energy (kJ mol^{-1})	Solvent	10^{-9} k_q/dm^3 mol^{-1} s^{-1} (number of acceptor concentrations)
Benzophenone (1)	535	289.5 [a]	Acetone	3.76 ± 0.07 (9)
2,5-Diphenyloxazole (2)	500	[b]	Methanol	1.84 ± 0.08 (10)
Riboflavin (3)	650	196.1 [c]	Water	1.44 ± 0.12 (9)
1-Chloroanthracene (4)	430	176.3 [a]	Methanol	0.94 ± 0.03 (8)
Eosin (5)	570	171.5 [d]	Water	1.13 ± 0.09 (8)
Erythrosin (6)	570	171.0 [e]	Water	1.41 ± 0.06 (8)
9,10-Dichloroanthracene (7)	420	169.2 [a]	Dioxan	0.312 ± 0.019 (9)
Naphthacene (8)	495	122.6 [f]	CH_2Cl_2	0.236 ± 0.036 (7)
Rubrene (9)	475	110.0 [g]	Benzene	<0.01 (2)
β-Carotene (10)	520	75 [h]	Acetone	<0.01 (7)

(b) Inorganic excited states

Donor	Analysing wavelength (absorption) (nm)	Excited state energy (kJ mol^{-1})	Solvent	10^{-9} k_q/dm^3 mol^{-1} s^{-1} (number of acceptor concentrations)
Uranyl nitrate (11)	510	245.2 [i]	Aq. $HClO_4$ (0.01M)	1.18 ± 0.06 (9)
$[Ru(bipy)_3]^{2+}$ (12)	580	204.8 [j]	Water	1.95 ± 0.04 (12)
$[Ru(phen)_3]^{2+}$ (13)	580	210.8 [j]	Water	2.13 ± 0.34 (9)
Bis-(8-hydroxyquinolinato)Pt^{II} (14)	656	185.6 [k]	Acetone	3.58 ± 0.20 (9)
$[Cr(phen)_3]^{3+}$ (15)	730	163.8 [l]	Aq. HCl (0.01M)	1.70 ± 0.06 (9)
$[Cr(bipy)_3]^{3+}$ (16)	733	163.2 [l]	Aq. HCl (0.01M)	1.39 ± 0.10 (9)

[a] S. L. Murov. 'Handbook of Photochemistry,' Dekker, New York, 1973, Section 2. [b] Unlisted in J. B. Birks, 'Photophysics of Aromatic Molecules,' Wiley, New York, 1970, vol. 1, or ref. 1*a*. [c] J. Posthuma and W. Berends, *Biochim. Biophys. Acta*, 1966, **112**, 422. [d] Ref. 19. [e] T. Ohno and S. Kato, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 3385. [f] G. Porter and M. W. Windsor, *Proc. R. Soc.* (*London*), 1958, *A*, **245**, 238. [g] W. G. Herkstroeter and P. B. Merkel, *J. Photochem.*, 1981, **16**, 331. [h] F. Wilkinson and A. Farmilo, *J. Chem. Soc., Faraday Trans. 2*, 1976, 604. [i] H. D. Burrows and T. J. Kemp, *Chem. Soc. Rev.*, 1974, **3**, 139. [j] J. N. Demas and G. A. Crosby, *J Am. Chem. Soc.*, 1976, **93**, 2841. [k] C. Bartocci, S. Sostero, O. Traverso, A. Cox, T. J. Kemp, and W. J. Reed, *J. Chem. Soc., Faraday Trans. 1*, 1980, 797. [l] N. A. P. Kane-Maguire and C. H. Langford, *Chem. Commun.* 1971, 895.

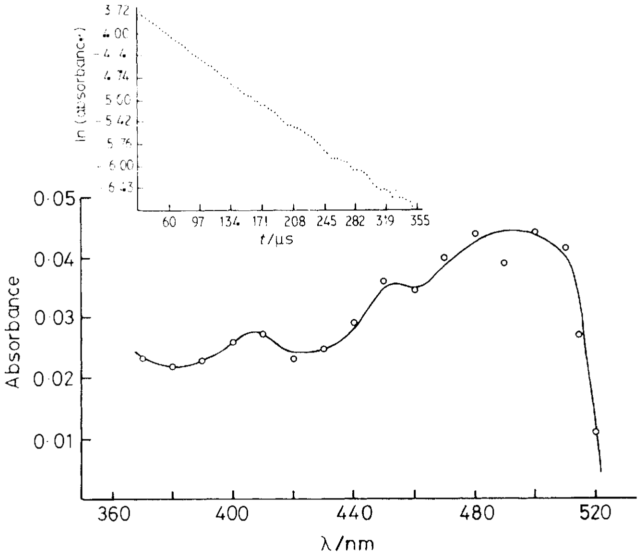


Figure 3. *T* – *T* absorption of rubrene (10^{-4} mol dm^{-3}) produced on pulse radiolysis of a deaerated solution in benzene containing biphenyl (0.1 mol dm^{-3}). Inset, decay of rubrene triplet at absorption maximum of 475 nm

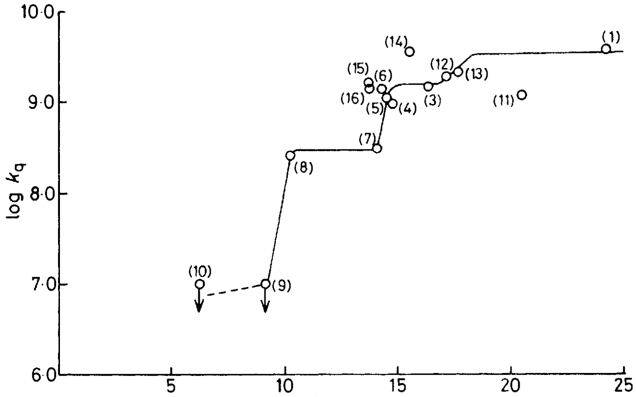


Figure 4. Plot of second-order quenching constant k_q against donor energy for quenching by (1a). Numbering key to quenchers as in Table 1.

Quenching of Excited States of Inorganic Species.—A wide variety of inorganic excited states [Tables 1(b) and 2, and Figure 1] are quenched very effectively by both (1a) and $Co(acac)_3$. There seems little relation between the reduction potential of the excited donor and k_q, thus E° for $[UO_2^{2+}]^*$, $[Ru(bipy)_3^{2+}]^*$, and $[Cr(bipy)_3^{3+}]^*$ are, respectively +2.60,[17a] +0.84,[17b] and +1.46 V [17b] while k_q for these donors vary by less than a factor of 2, and a mechanism of electron-transfer to give the known [18] transient species $[RCo^{IV}(dmgH)_2(H_2O)]^+$ can probably be ruled out in favour of one of simple energy transfer. The values of k_q for inorganic quenchers are also included in the Wilkinson plots (Figures 4 and 5); although such inclusion disregards spin-statistical effects [10] on k_q, the

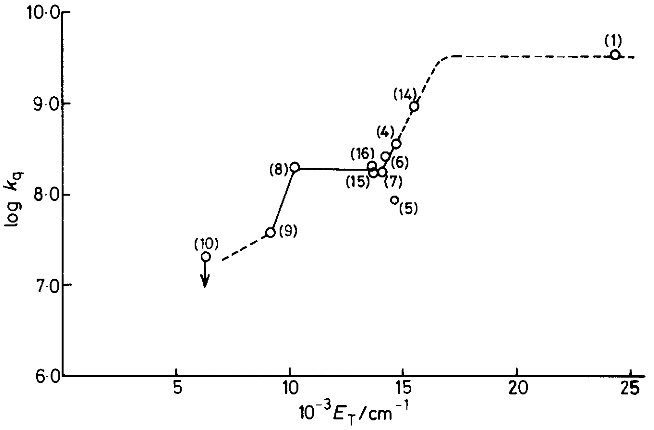


Figure 5. Plot of second-order quenching constant k_q against donor energy for quenching by Co(acac)$_3$. Numbering key as in Table 1

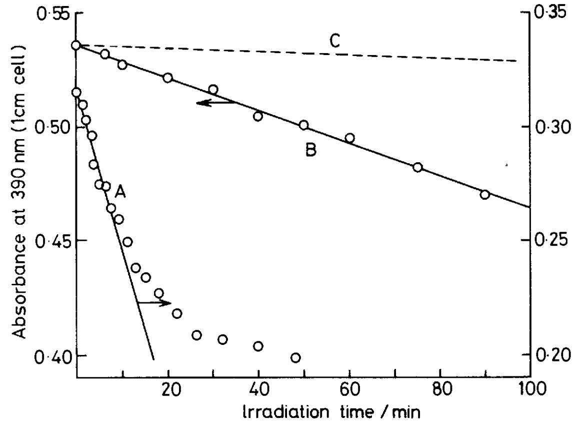


Figure 6. Sensitization of the photodecomposition of (1a) by erythrosin. A, Direct photolysis (547 nm) of (1a) (2.0 × 10^{-4} mol dm^{-3}) in a 5 cm cell in aqueous buffer (pH 5.00 ± 0.05) monitored at 390 nm in a 1 cm cell. B, Photolysis (547 nm) of a solution containing (1a) (2.0 × 10^{-4} mol dm^{-3}) and erythrosin (4.0 × 10^{-4} mol dm^{-3}), *i.e.* with O.D.$_{547}$ erythrosin/O.D.$_{547}$ (1a) = 124. C, Component of photolysis B attributable to *direct* photolysis of (1a)

Table 2. Quenching of excited states by Co(acac)$_3$

Donor[a]	Solvent	$10^{-9}k_q$/dm^3 mol^{-1} s^{-1} (number of acceptor concentrations)
(1)	Acetone	3.26 ± 0.23 (9)
(4)	Methanol	0.35 ± 0.01 (10)
(5)	Methanol	0.103 ± 0.006 (9)
(6)	Methanol	0.26 ± 0.02 (8)
(7)	Dioxan	0.173 ± 0.01 (9)
(8)	CH$_2$Cl$_2$	0.195 ± 0.02 (7)
(9)	Benzene	0.0360 ± 0.0031 (4)[b]
(10)	Acetone	<0.02 (7)
(14)	Acetone	0.89 ± 0.05 (9)
(15)	Acetone	0.167 ± 0.01 (7)
(16)	Acetone	0.197 ± 0.02 (7)

[a] For key to numbering, see Table 1. [b] Three determinations were made at each concentration.

overall trend clearly covers both organic and inorganic donors.

Methylcobalamin behaves much as (1a) in exhibiting powerful quenching of the lifetimes both of typical organic and inorganic donors; thus the $T - T$ absorption of eosin in MeOH solution is quenched at a rate of (3.72 ± 0.16) × 10^8 dm^3 mol^{-1} s^{-1} while the phosphorescence of [Cr(phen$_3$)]$^{3+}$ in aqueous HCl (0.01M) is quenched at a rate of (1.28 ± 0.08) × 10^8 dm^3 mol^{-1} s^{-1}.

Sensitization of the Photodecomposition of (1).—The foregoing results having indicated (1a) to be a powerful quencher of a wide variety of excited states, we explored the possibility of sensitization of the decomposition of (1a) by organic triplet states. When an aqueous buffered (pH 5.00 ± 0.05) solution of (1a) (2.0 × 10^{-4} mol dm^{-3}) was irradiated at 547nm in a 5 cm cell (with O.D.$_{547}$ = 0.050), (1a) was photodecomposed quite rapidly with an initial rate of 1.175 × 10^4 O.D. units (390 nm) cm^{-1} s^{-1}, *i.e.* 8.64 × 10^{-8} mol dm^{-3} s^{-1}. Irradiation of a 2.0 × 10^{-4} mol dm^{-3} solution of (1a) under identical conditions in the presence of erythrosin (4.0 × 10^{-4} mol dm^{-3}) with O.D.s at 547 nm (5 cm cell) of 0.050 (1a) and 6.21 (erythrosin) gave ΔO.D./Δt at 390 nm of -1.210×10^{-5} O.D. units s^{-1} (Figure 6). Now since the inner filter effect of the erythrosin means that at 547 nm, the ratio of light absorbed by (1a) is 0.0080 (or 0.80%), then *direct* photolysis of (1a) is responsible for only 0.80% of -1.75×10^{-4} O.D. units (390 nm) s^{-1}, *i.e.* -9.4×10^{-7} O.D. units (390 nm) s^{-1}. This indicates that 92.2% of the decompositions of (1a) is sensitized by erythrosin. In another set of experiments under similar conditions that the fraction sensitized was 91.3%. (We established under the conditions utilised, erythrosin underwent photolysis only very slowly at 547 nm, *i.e.* 4.8% in 80 min irradiation.)

A similar procedure was followed with eosin as potential donor. Irradiation of (1a) (2.0 × 10^{-5} mol dm^{-3}; 5 cm cell; pH 5.00 ± 0.05) with light of 498 nm wavelength induced ready photolysis of (1a) with ΔO.D.$_{390}$/Δt – 7.83 × 10^{-5} s^{-1}. Irradiation under identical conditions but in the presence of eosin (2.0 × 10^{-5} mol dm^{-3}) gave ΔO.D.$_{390}$/Δt – 2.18 × 10^{-5} s^{-1}. Since, at 498 nm, O.D.(eosin)/O.D.(1a) was 164, the fraction of light absorbed by (1a) was 0.61%, and the direct photolysis of (1a) accounted for ΔO.D./Δt – 4.78 × 10^{-7} s^{-1}: thus sensitization by eosin accounted for 97.0% of the decomposition of (1a). (Irradiation of eosin under these experimental conditions gave only slight photodecomposition.)

To dissolve Crystal Violet, $\lambda_{max.}$ 586 nm, ($\varepsilon_{max.}$ 1.031 × 10^5 dm^3 mol^{-1} cm^{-1}), E_T 175.7 kJ mol^{-1},[19] appreciably, solutions were adjusted to pH 2.0. Photolysis of (1a) (4.0 × 10^{-5} mol dm^{-3}) in a perchlorate medium at 547 nm gave ΔO.D.$_{390}$/Δt 1.59 × 10^{-4} s^{-1} [φ(–1a) is known to increase as pH is reduced [7a]]. Irradiation (547 nm) of a solution containing (1a) (4.0 × 10^{-5} mol cm^{-3}) and Crystal Violet (6.0 × 10^{-5}) gave ΔO.D.$_{390}$/Δt = 6.92 × 10^{-5} s^{-1}: under these conditions O.D.$_{547}$ (Crystal Violet)/O.D.$_{547}$ (1a) = 86 : 1, and it can be shown that sensitization accounts for 97.4% of the observed photolysis. This result complements those of Table 1 inasmuch as Crystal Violet gave an insufficiently intensely absorbing transient on ns flash photolysis to enable direct kinetic studies of its quenching by (1a). [In another run, 4.0 × 10^{-5} mol dm^{-3} Crystal Violet was used, when ΔO.D.$_{390}$/Δt was 6.45 × 10^{-5} s^{-1}, O.D.$_{547}$ (Crystal Violet)/O.D.$_{547}$ (1a) was 63 : 1, and sensitization accounted for 95.4% of the photodecomposition of (1a).] This result is slightly less clearcut than those found with eosin and erythrosin in that the sensitizing dye underwent appreciable photolysis at 547 nm, pH 2.0 (*ca.* 10% during the first 12 min, the typical duration of a sensitization experiment).

When 1-chloranthracene was used as potential sensitizer, it was necessary to monitor changes in [(1a)] at 447 nm while irradiating at 363 nm. Irradiation of (1a) in MeOH (2.0 × 10^{-5} mol dm^{-3}) led to its ready decomposition with ΔO.D.$_{447}$/Δt 3.16 × 10^{-4} s^{-1}, while the presence of 1-chloranthracene (4.0 × 10^{-4} mol dm^{-3}), when O.D.$_{363}$(1-chloranthracene)/

O.D.$_{363}$(1a) = 54 : 1, gave ΔO.D.$_{447}/\Delta t$ 3.96×10^{-5} s^{-1}. Of this irradiation, 1/55 parts may be attributed to direct photolysis at 363 nm, *i.e.* to 5.75×10^{-6} s^{-1}, which is 14.5% of the total rate in the sensitized photolysis: the remaining 85.5% is therefore sensitized.

Another type of experiment concerned an attempt to observe energy transfer *from* (1a)* *to* a low-energy acceptor, namely Methylene Blue which has E_T 139.2 kJ mol^{-1}.[20] Irradiation at 401 nm of (1a) (5.0×10^{-5} mol dm^{-3} in 0.1M-aqueous H_2SO_4), gave rapid loss of (1a) with ΔO.D.$_{390}/\Delta t$ 2.52×10^{-4} s^{-1}. In the presence of Methylene Blue (1.0×10^{-5} mol dm^{-3}), the figure was 2.04×10^{-4} s^{-1}, but correction for the few percent of light internally filtered by the dye increases this to 2.20×10^{-4} s^{-1}. At a dye concentration of 1.0×10^{-4} mol dm^{-3}, the figure was 1.05×10^{-4} s^{-1}, but the (now large) correction for inner filtering by Methylene Blue increases this to 2.29×10^{-4} s^{-1}. Considering the inherent errors in these experiments, we consider the results to indicate that 10^{-4}M-Methylene Blue fails to protect excited (1a) from decomposition by energy transfer.

Discussion

It is quite clear from Tables 1 and 2 and Figures 1, 2, 4, and 5 that alkylcobalt(III) compounds are highly effective quenchers both of organic triplet states and of a variety of excited inorganic species. This covers n-π* and π-π* states in the organic series, provided E_T exceeds *ca.* 170 kJ mol^{-1}, and inorganic species with excited state reduction potentials[17] spanning the range +0.74 V for [Ru(bipy)$_3^{2+}$]* to +2.60 V for [UO$_2^{2+}$]*. The very high values for k_q indicate the process to be one of energy transfer throughout the series, and this view is supported by the much lower quenching efficiencies, both by (1a) and Co(acac)$_3$, towards the donors of lower triplet energy (naphthacene, rubrene, and β-carotene and, to a lesser extent, 9,10-dichloroanthracene).

The role of energy transfer is supported by spectral measurements during photosensitization experiments: in all cases simple photodecomposition of (1a) appeared to take place to give [Co(H$_2$O)$_6$]$^{2+}$, free ligand, and alkyl ligand-derived products, rather than the semi-reduced or semi-oxidized species [reactions (2)—(6)]. In the case of Co(acac)$_3$, the analogue of reaction (6) is of minor importance. Although a number of organic triplet donors have been used to photodecompose Co^{III} complexes,[8] rather few attempts have been made to assess the energy requirements of the sensitization process. Interestingly, while benzophenone and 2-acetonaphthone triplets sensitize the redox decomposition of Co(dtp)$_3$ (dtp$^-$ = EtOPS$_2$), benzil triplet fails in this respect, indicating the dissociative level to lie at *ca.* 247 kJ mol^{-1}, *cf.* the lowest energy charge-transfer band at 294 kJ mol^{-1}.[21]

$$\mathrm{D} \xrightarrow{h\nu} {}^1\mathrm{D}^* \qquad (2)$$

$$ {}^1\mathrm{D}^* \xrightarrow{\text{i.s.c.}} {}^3\mathrm{D} \qquad (3)$$

$$ {}^3\mathrm{D} + (1a) \longrightarrow {}^1\mathrm{D} + (1a)^* \qquad (4)$$

$$ (1a)^* \longrightarrow (1a) \qquad (5)$$

$$ (1a)^* \longrightarrow \mathrm{R}\cdot + \mathrm{Co}^{2+} + 2\,\mathrm{dmgH} + \mathrm{H_2O} \qquad (6)$$

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