Quenching of Excited Uranyl Ion by Metal Carbonyls in Aprotic Solvents

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The nature of the quenching of the luminescent state of uranyl ion by a number of metal carbonyls, $[M(CO)_n]$, has been studied in aprotic solvents. Flash photolysis and e.s.r. and i.r. spectroscopy show that the quenching process takes place with concomitant formation of the paramagnetic reactive intermediate, $[M(CO)_n]^+$, and the $[UO_2]^+$ ion. The bimolecular quenching constants k_Q are related to the free energy change of the electron-transfer process; thus values of log k_Q are correlated with the oxidation potentials of $[M(CO)_n]$. The primary photoproducts are involved subsequently in an irreversible redox process with formation of U^{IV} and M^{z+} ions.

THE uranyl ion $[UO_2]^{2+}$ luminesces ($\lambda_{max.}$ 510 nm) in fluid solutions at room temperature,[1,2] thereby providing a ready means for the study of a variety of bimolecular excited-state processes. In several cases, however, this approach is complicated by the fact that uranyl ion forms ground-state complexes with a variety of chemical species, so that it is often difficult to distinguish between intramolecular photochemical processes involving uranyl ion–ligand complexes[3] and intermolecular photochemical processes involving reaction between electronically excited $[UO_2]^{2+}$ and substrate.[2-4]

To provide a clearer understanding of the possible mechanisms in the quenching of emission from $(UO_2^{2+})^*$, we have selected as quenchers organometallic compounds having no co-ordinative tendency with uranyl ion. We have recently reported on the quenching of $(UO_2^{2+})^*$ by d^6 metallocenes,[4] which clearly indicated the role of simple electron transfer from quencher to $(UO_2^{2+})^*$: we were intrigued to determine whether this mechanism extended to metal carbonyls such as $[Cr(CO)_6]$, which would imply intermediacy of the rather elusive $[M(CO)_n]^+$ species.

EXPERIMENTAL

Materials.—Uranyl nitrate was of AnalaR quality. Acetone was Merck Spectro material that was further purified before use by vacuum distillation from P_4O_{10}. Acetonitrile (Merck Spectro quality) was further purified by the method of O'Donnell *et al.*[5] Tetrahydrofuran (Merck Spectro quality) was purified by successive fractional distillations, under nitrogen, from $Li[AlH_4]$. All the solvents were stored under nitrogen in the dark and in a dry-box. The metal carbonyls were obtained from Alfa Inorganics and were generally used without further purification.

Apparatus.—Luminescence spectra were recorded on a Perkin-Elmer MPF-2A spectrofluorimeter at excitation and emission wavelength settings of 410 and 510 nm respectively.

Measurements of the luminescence lifetime were made with a frequency-doubled model K-347 ruby laser (λ 347 nm) (J. K. Lasers Ltd.). Pulses were of *ca.* 50 ns duration and the emission of $(UO_2^{2+})^*$ was monitored at 510 nm and kinetic decays were recorded with a Polaroid camera. Microsecond flash-photolysis experiments were performed on a model KR-10 Flash-Kinetic Spectrophotometer (Applied Photophysics Ltd.). E.s.r. experiments were carried out with a Bruker model ER 200tt spectrometer and i.r. and electronic spectra were recorded on Perkin-Elmer 577 and 323 recording spectrometers respectively.

Our customary procedure was used to obtain radiation wavelengths of 404 and 433 nm.[6] Irradiations were performed using 1-cm pathlength quartz cells filled with solution (3 cm³) and housed in suitable cell holders. The incident light intensity was measured by means of the potassium tris(oxalato)ferrate(III) actinometer, and it was of the order of 2×10^{-7} einstein s^{-1} (1 einstein = $N_0h\nu$ J mol^{-1}).

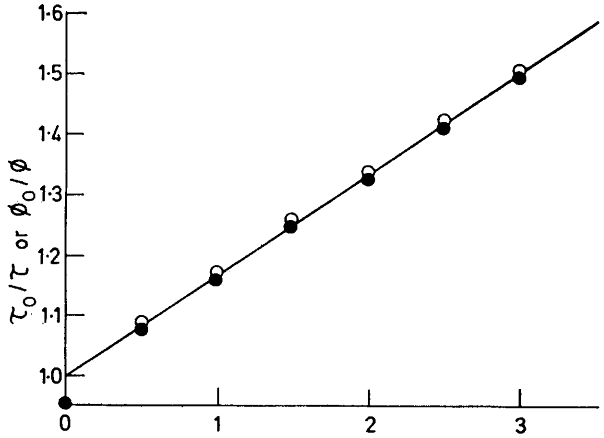

FIGURE 1 Quenching of uranyl luminescence by $[Cr(CO)_6]$ at 298 K: (○) luminescence intensity; (●) lifetime, τ, of $(UO_2^{2+})^*$

Procedure.—*Quenching studies.* Solutions of $[UO_2]^{2+}$ at a constant concentration (5×10^{-3} mol dm^{-3}) and the quencher were placed in a quartz cell and degassed by freeze–pump–thaw cycles. The luminescence spectrum of each sample was measured and the relative emission yields determined as a function of quencher concentration. The luminescence spectrum of $[UO_2]^{2+}$ was unaffected by the presence of any quenchers examined. All the quenching data were expressed in the form of the Stern–Volmer plot, the gradient of which yields K_{SV}. The absolute quenching constant (k_Q) can be determined from K_{SV}, which equals $k_Q\tau_0$, after determination of τ_0 the lifetime of $(UO_2^{2+})^*$ in the presence of quencher Q. Lifetime data are also expressed in the form of the Stern–Volmer plot, $\tau_0/\tau = 1 + K_{SV}[Q]$.

RESULTS

Emission Intensity and Lifetime Measurements.—A variety of metal carbonyls was used as quenchers of $(UO_2^{2+})^*$ and in all cases except $[V(CO)_6]$ the quenching follows strictly Stern–Volmer kinetics, *e.g.* Figure 1. Quenching constants were obtained by determination of the emission lifetimes of $(UO_2^{2+})^*$ at variable quencher concentration, *e.g.* Figure 1. Quantitative results are given in Table 1.

TABLE 1

Quenching rates of $(UO_2^{2+})^*$ by metal carbonyls

Quencher	Lowest $\tilde{\nu}_{max.}$/ 10^3 cm^{-1} [a]	k_Q/dm^3 mol^{-1} s^{-1}
(1) $[Ni(CO)_4]$	42.27	$(1.55 \pm 0.10) \times 10^8$
(2) $[Fe(CO)_5]$	40.00	$(4.80 \pm 0.05) \times 10^7$
(3) $[W(CO)_6]$	28.30	$(4.15 \pm 0.04) \times 10^7$
(4) $[Mo(CO)_6]$	28.85	$(4.15 \pm 0.04) \times 10^7$
(5) $[Cr(CO)_6]$	29.50	$(4.15 \pm 0.04) \times 10^7$
(6) $[Mn_2(CO)_{10}]$	29.40	$(3.82 \pm 0.03) \times 10^7$
(7) $[V(CO)_6]$	28.00	$(5.8 \pm 0.2) \times 10^4$

[a] From M. Wrighton, *Chem. Rev.*, 1974, **74**, 401.

Microsecond Flash Photolysis.—On flash photolysis ($\lambda >$ 380 nm) of the quenched systems of Table 1, efficient immediate bleaching ($400 \leqslant \lambda \leqslant 600$ nm) of the $[UO_2]^{2+}$ absorption was observed. The spectral distribution of the bleaching is consistent with the production of $[UO_2]^+$, but inconsistent with the production of a uranium(IV) species.[4,6]

E.S.R. Measurements.—Irradiation (λ 404 nm, $\pi_u \rightarrow 5f$ excitation) of an e.s.r. cavity containing a sample of a carefully degassed solution of $[Cr(CO)_6]$ and uranyl nitrate (5×10^{-2} mol dm^{-3}), at which concentration light absorption by metal carbonyl is negligible, led to a spectrum with a single broad line centred at $g = 1.843$, clearly indicating induced oxidation of $[Cr(CO)_6]$ to the reactive 17-electron cation $[Cr(CO)_6]^+$ from the agreement with the e.s.r. spectrum obtained during electrochemical oxidation of $[Cr(CO)_6]$.[7] Under continuous photolysis the intensity of the signal increases until a steady state is reached, but on interruption of the irradiation it quickly decays to a zero level.

U.v. Changes.—Whilst irradiation of degassed solutions of uranyl nitrate (5×10^{-2} mol dm^{-3}) in anhydrous acetone or acetonitrile with visible light (λ 404 and 433 nm) caused no appreciable reaction, photolysis at 433 nm of solutions containing uranyl nitrate (5×10^{-2} mol dm^{-3}) and metal carbonyls (10^{-2} mol dm^{-3}) listed in Table 1 generates a new absorption band with $\lambda_{max.}$ 640 nm, which coincides with that established for U^{IV}.[4,8]

I.r. Changes.—The spectra of the photolysed solutions at the end of prolonged photolysis (3 h) showed no absorption peaks due to carbonyl-containing species.

DISCUSSION

The experimental results clearly show that a variety of metal carbonyls in aprotic solvents are strong quenchers of $(UO_2^{2+})^*$ emission. The quenching constants obtained from measurements of luminescence intensity agree with those obtained from luminescence lifetimes (Figure 1), indicating a dynamic quenching mechanism. For these systems, quenching by either an external heavy-atom effect or spin-catalysed deactivation is unlikely, in view of the fact that $[UO_2]^{2+}$ already contains a heavy atom and has a poorly defined spin number. Either energy or electron transfer therefore remain the most plausible quenching mechanisms. Comparison of the excited-state energy[9] (20 500 cm^{-1}) and the excited-state reduction potential[9] (2.6 V) of $(UO_2^{2+})^*$ with the energy of the lowest excited state of the quenchers (Table 1) shows that for all the quenchers only electron transfer is energetically allowed. With the exception of $[V(CO)_6]$ (for which there is no $E^{\ominus}$ value),[7] an almost linear correlation was found for log k_Q against $E^{\ominus}$, the primary oxidation potential of the metal carbonyl (Figure 2); Figure 2 also includes some typical data for quenching of $(UO_2^{2+})^*$ by metallocenes taken from ref. 4. This indicates that electron transfer is the dominant mechanism. Comparison (Table 2) of the $(UO_2^{2+})^*/[UO_2]^+$ reduction potential and the standard electrode potentials of metal carbonyls[7] shows that electron-transfer quenching is thermodynamically allowed: indeed $\Delta G_Q^{\ominus} = E_Q^{\ominus} - E_Q(UO_2^{2+})^*$ is always more negative than -1.05 V. Compared to the quenching constants of the other metal carbonyls (Table 1), $[V(CO)_6]$ has a low value for k_Q. This suggests that d^5 $[V(CO)_6]$ (which is, of course, not isoelectronic with the other mononuclear carbonyls) has a relatively high oxidation potential. Consistent with this interpretation is the fact that neither chemical nor electrochemical oxidation products of $[V(CO)_6]$ have been reported.[7] However, analysis of the i.r. and electronic spectra of the $[UO_2]^{2+}$–$[V(CO)_6]$ solution at the end of the photolysis, together

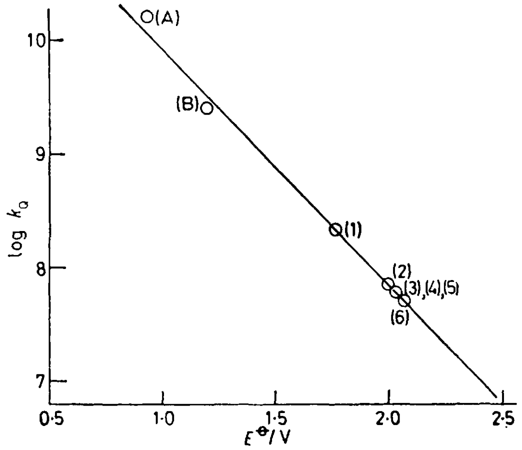

FIGURE 2 Correlation of log k_Q and $E^{\ominus}$ (metal carbonyl) for quenching of $(UO_2^{2+})^*$ luminescence by the carbonyls in Table 1. (A) and (B) refer to $E^{\ominus}$ for Fe$[(\eta\text{-}C_5H_5)_2]$ and $[Ru(\eta\text{-}C_5H_5)_2]$ from ref. 4

TABLE 2

Free-energy changes in the electron-transfer process between $(UO_2^{2+})^*$ and metal carbonyls

Metal carbonyl	$E^{\ominus}$/V [a]	$-\Delta G_Q$/V
(1)	1.26	1.34
(2)	1.51	1.09
(3)	1.53	1.07
(4)	1.53	1.07
(5)	1.53	1.07
(6)	1.55	1.05

[a] Taken from ref. 7.

with the flash-photolysis behaviour, indicates that $[V(CO)_6]$ does indeed undergo the same sensitised oxidation as the other carbonyls.

In agreement with the above correlations, both flash-photolysis experiments and e.s.r. and i.r. spectral profiles of the photoreactions clearly indicate formation of transient redox intermediates {*i.e.* $[UO_2]^+$ and $[Cr(CO)_6]^+$} as primary photoproducts. Both the lack of a dependence of k_Q on solvent polarity and the absence of any evidence for exciplex emission in our systems support an outer-sphere electron-transfer reaction, which involves only the transfer of one electron without any bond-making or bond-breaking processes. Thus, in view of the powerful oxidising properties of $(UO_2^{2+})^*$,[4,9] and the spectral characteristics of the photoproducts, we propose an oxidative excited-state electron-transfer model:

$$(UO_2^{2+})^* + Q \xrightarrow{k_Q} [UO_2]^+ + Q^+$$

where Q and Q^+ are metal carbonyls and metal carbonyl cations respectively, and k_Q is the normal bimolecular quenching constant. The electron-transfer mechanism can be described by the scheme in equations (1)—(5)

$$[UO_2]^{2+} + h\nu \xrightarrow{I_a} (UO_2^{2+})^* \qquad (1)$$

$$(UO_2^{2+})^* \xrightarrow{k_F} [UO_2]^{2+} + h\nu_F \qquad (2)$$

$$(UO_2^{2+})^* \xrightarrow{k_D} [UO_2]^{2+} + \text{heat} \qquad (3)$$

$$(UO_2^{2+})^* + Q \xrightarrow{k_4} [UO_2]^+ + Q^+ \qquad (4)$$

$$(UO_2^{2+})^* + Q \xrightarrow{k_5} [UO_2]^{2+} + Q + \text{heat} \qquad (5)$$

where I_a = absorbed light intensity. Using the Stern–Volmer relation and the steady-state approximations for $(UO_2^{2+})^*$, equation (6) can be obtained where $\tau_0 = 1/(k_F + k_D)$, *i.e.* we can write (7).

$$I_{F^0}/I_F = 1 + \tau_0(k_4 + k_5)[Q] \qquad (6)$$

$$K_{SV} = \tau_0(k_4 + k_5) \qquad (7)$$

Electronic and i.r. spectral profiles or the photoreactions showed no evidence for *stable* cationic carbonyls, and this is not surprising since these species are very susceptible to nucleophilic attack {*cf.* the transient character of the e.s.r. absorption of $[Cr(CO)_6]^+$ in our experiments}. The formation of uranium(IV) species, together with the lack of any evidence in the i.r. spectra for carbonyl species in the late stages of photoreactions, indicates that in all cases the primary photoproducts, *i.e.* $[UO_2]^+$ and Q^+, are involved in subsequent irreversible redox processes, *e.g.* (8) with n = 4—6. Consistent with this interpretation is the ready reduction of $[UO_2]^+$ to U^{IV}.[10] $[M(CO)_n]^+$ is itself unstable with respect to disproportionation. The k_Q values in Table 1 demonstrate the high efficiency of $(UO_2^{2+})^*$ in oxidising metal carbonyls. The striking similarity in the k_Q values for the carbonyls of the Group 6B metals probably arises because the electron is removed from non-bonding orbitals in the three metals with closely similar energies. Consistent with this view are both molecular-orbital calculations and ionisation potentials obtained by mass spectroscopy.[11]

$$[UO_2]^+ + [M(CO)_n]^+ \longrightarrow U^{IV} + M^{2+} + nCO \qquad (8)$$

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