Temperature Independent Ru → Os Electronic Energy Transfer in a Rodlike Dinuclear Complex with a 2.4 nm Intermetal Separation

Leif Hammarström,*,†,‡,§ Francesco Barigelletti,*,†
Lucia Flamigni,† Nicola Armaroli,† Angelique Sour,||
Jean-Paul Collin,*,|| and Jean-Pierre Sauvage*,||

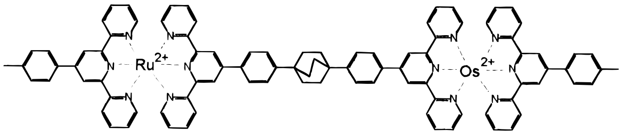
Istituto FRAE-CNR, Via Gobetti 101
I-40129 Bologna, Italy
Dipartimento di Chimica "G. Ciamician"
Università di Bologna
Via Selmi 2, I-40126, Bologna, Italy
Department of Physical Chemistry, University of Uppsala
Box 532, S-75121 Uppsala, Sweden
Laboratoire de Chimie Organo-Minerale
Université Louis Pasteur, Faculté de Chimie
1 rue Blaise Pascal, F-67008 Strasbourg, France

Received July 8, 1996

The development of molecular wires or rods where photoactive and electroactive termini are linked by large-size bridging molecular units may open new paths in the field of storage and utilization of light energy.[1] In such types of molecular species, it should in fact be possible to drive electron and/or energy transfer processes over nanometer distances by the use of light. This is an appealing perpective for the development of molecular machineries,[2] as well as for studies of the role played by energetic and electronic factors within the framework of current theories.[3] In rigid rodlike species, the key role played by the bridge is 2-fold, because (i) it gives the desired rigidity to the molecular backbone by fixing the distance and, to a certain extent, the relative orientation between the reacting centers and (ii) it can contain different molecular subunits with either conducting or isolating electronic properties. The latter point is of importance in view of the tunability of the photoinduced processes,[1,2] and recent reports deal with the preparation of molecular wires which include a great variety of bridges.[4]

Studies concerning the effect of temperature on electron transfer processes occurring in homogeneous polar media have demonstrated that electron transfer can be blocked in frozen solvent, if the process is not exothermic enough.[5] This may be explained by the fact that solvent reorganization cannot take place in rigid matrices, and the products are therefore energetically destabilized in comparison with the fluid case. Regarding energy transfer, systematic studies on the effect of temperature and state of the solvent are scarce,[6] even if it has already been noted that vitrification of the medium exerts a relatively small influence on the energy transfer process.[7]

Scheme 1



(ttp)Ru(tpy-ph-bco-ph-tpy)Os(ttp)$^{4+}$

In this paper we show that energy transfer in a rodlike dinuclear complex, (ttp)Ru(tpy-ph-bco-ph-tpy)Os(ttp)$^{4+}$ (RuOs) (Scheme I), is unaffected both by temperature and state of the solvent {tpy = 2,2′:6′,2″-terpyridine, ttp = 4′-*p*-tolyl-tpy, ph = 1,4-phenylene, bco = bicyclo[2.2.2]octane}.

In this species the coordination environment of both metals consists of tpy-type tridentate ligands,[8] and the spacer is a ph-bco-ph fragment. The complex exhibits a rigid, linear geometry, and the metal-to-metal distance is fixed at 2.4 nm.[9]

Visible light absorption of dilute solutions of the RuOs complex[10] at 490 nm produces Ru- and Os-based metal-to-ligand charge transfer triplet excited states (^{3}MLCT) in a 1:1 ratio, and the Ru → Os energy transfer is thermodynamically allowed, $\Delta G° = -0.26$ eV.[11] Energy transfer may be conveniently monitored by comparing the Ru-based luminescence lifetime in RuOs (τ) with that of the reference complex Ru(ttp)$_2^{2+}$ (Ru) (τ_o) (eq 1).[12]

$$k_{en} = 1/\tau - 1/\tau_o \qquad (1)$$

We have therefore measured the Ru-based luminescence lifetimes for the two complexes in butyronitrile, in the temperature interval from 90 to 293 K (Figure 1). Our results can be summarized as follows.

(i) High Temperature Behavior. At room temperature, the Ru-based luminescent excited states of RuOs and Ru exhibit the same lifetime value, 1.2 ns. For the dinuclear complex, this indicates that the Ru → Os energy transfer is too slow (*vide infra*) to compete with intrinsic Ru-based deactivation.

(ii) Changes with Temperature. We have analyzed the temperature dependent emission lifetime data for RuOs and Ru according to eq 2.

[†] Instituto FRAE-CNR.

[‡] Università di Bologna.

[§] University of Uppsala.

[||] Université Louis Pasteur.

(1) (a) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163. (b) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435. (c) Fox, M. A.; Jones, W. E., Jr.; Watkins, D. M. *Chem. Eng. News* **1993**, *71*, 38. (d) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **1993**, *26*, 198.

(2) Balzani, V.; Scandola, F. In *Comprehensive Supramolecular Chemistry*; Reinhout, D. N., Ed.; Pergamon: Oxford, 1996, Vol. 10, p 1.

(3) (a) Marcus, R. A.; Sutin, N. *Biochem. Biophys. Acta* **1985**, *811*, 265. (b) See: *Chem. Phys.* **1993**, *176*, 1−640 and *Chem. Rev.* **1992**, *92*, 364−490. (c) Balzani, V.; Bolletta, F.; Scandola, F. *J. Am. Chem. Soc.* **1980**, *102*, 2152. (d) Sigman, M. E.; Closs, G. L. *J. Phys. Chem.* **1991**, *95*, 5012. (e) Murtaza, Z.; Graff, D. K.; Zipp, A. P.; Worl, L. A.; Jones, W. E., Jr.; Bates, W. D.; Meyer, T. J. *J. Phys. Chem.* **1994**, *98*, 10504.

(4) For a recent review, see: (a) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serrone, S. *Chem. Rev.* **1996**, *96*, 759. (b) Grosshenny, V.; Harriman, A.; Ziessel, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2705. (c) Belser, P. *Chimia* **1993**, *48*, 347.

(5) For example, see: (a) Gaines, G. L., III; O'Neil, M. P.; Svec, W. A.; Niemczyk, M. P.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1991**, *113*, 719. (b) Scandola, F.; Argazzi, R.; Bignozzi, C. A.; Indelli, M. T. *J. Photochem. Photobiol. A* **1994**, *82*, 191. (c) Collin, J.-P.; Guillerez, S.; Sauvage, J.-P.; Barigelletti, F.; De Cola, L.; Flamigni, L.; Balzani, V. *Inorg. Chem.* **1992**, *31*, 4112.

(6) Ryu, C. K.; Schmehl, R. H. *J. Phys. Chem.* **1989**, *93*, 7961. In this work the temperature dependence of energy transfer in a dinuclear Ru complex was measured between 200 and 300 K (i.e., exclusively in the fluid solvent region).

(7) Recent examples include: (a) Grosshenny, V.; Harriman, A.; Ziessel, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1100. (b) Indelli, M. T.; Scandola, F.; Collin, J.-P.; Sauvage, J.-P.; Sour, A. *Inorg. Chem.* **1996**, *35*, 303. (c) Barigelletti, F.; Flamigni, L.; Guardigli, M.; Juris, A.; Beley, M.; Chodorowski-Kimmes, S.; Collin, J.-P.; Sauvage, J.-P. *Inorg. Chem.* **1996**, *35*, 136.

(8) Sauvage, J.-P.; Collin, J.-P.; Chambron, J.-C.; Guillerez, S.; Coudret, C.; Balzani, V.; Barigelletti, F.; De Cola, L.; Flamigni, L. *Chem. Rev.* **1994**, *94*, 993.

(9) Barigelletti, F.; Flamigni, L.; Balzani, V.; Collin, J.-P.; Sauvage, J.-P.; Sour, A. *New J. Chem.* **1995**, *19*, 793. The complex was prepared as the hexafluorophosphate salt.

(10) The optical absorption spectrum of RuOs was the sum of the spectra of the reference components Ru(ttp)$_2^{2+}$ (Ru) and Os(ttp)$_2^{2+}$ (Os). Samples were $\sim 10^{-5}$ M in butyronitrile solvent, deaeration was accomplished at a vacuum line through repeated freeze−thaw pumping cycles.

(11) Valve estimated from 77 K luminescence band maxima of Ru and Os complexes (630 and 728 nm, respectively); for RuOs, two band maxima were registered at these same wavelengths. The luminescence spectra were obtained with a Spex Fluorolog II spectrofluorimeter. The uncertainty on the band maximum was ±2 nm. The room temperature luminescence quantum yield for Ru was $\Phi = 3.5 \times 10^{-5}$.[8]

(12) On the basis of $1/\tau_o = k_r + k_{nr}$ and $1/\tau = k_r + k_{nr} + k_{en}$, where r and nr stand for radiative and nonradiative processes, respectively. Lifetimes were measured either by employing a Continuum PY62-10 Nd:YAG laser with a Hamamatsu C1587 streak camera (room temperature) or IBH single-photon counting equipment; temperature control was achieved with a Thor Research cryostat, calibrated and home-modified to host quartz cuvettes. See: Beley, M.; Chodorowsky, S.; Collin, J.-P.; Sauvage, J.-P.; Flamigni, L.; Barigelletti, F. *Inorg. Chem.* **1994**, *33*, 2543.

S0002-7863(96)02333-5 CCC: $12.00

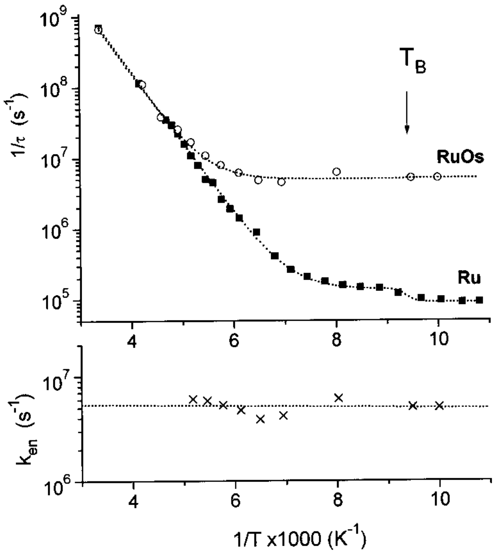


Figure 1. Temperature dependence of the time-resolved luminescence observed at $\lambda = 630-640$ nm for $Ru(ttp)_2^{2+}$ (Ru) and $(ttp)Ru(tpy\text{-}ph\text{-}bco\text{-}ph\text{-}tpy)Os(tpy)^{4+}$ (RuOs) (top) and of the rate of Ru → Os energy transfer in RuOs (bottom), see text. Dotted curves on top panel were obtained by fitting eq 2 to the experimental data points. The straight line on bottom panel is the result of a linear least-squares fitting. The glass-to-fluid temperature region of the butyronitrile solvent is centered around $T_B = 110$ K.

$$1/\tau = A \exp\left(-\frac{\Delta E}{RT}\right) + k_o \qquad (2)$$

As shown by many investigations dealing with the photophysics of Ru-polypyridine complexes, A and ΔE are the preexponential factor and the activation energy, respectively, for thermal population of a metal-centered (MC) state which is responsible for fast deactivation of the ^{3}MLCT luminescent state.[13,14] k_o is a low-temperature limiting rate, and for Ru, it includes the term $B/\{1 + \exp[C(1/T - 1/T_B)]\}$,[15] which takes care of effects concerned with the glass-to-fluid transition region of the solvent ($T_B \approx 110$ K, Figure 1). For $(ttp)Ru(tpy\text{-}ph\text{-}bco\text{-}ph\text{-}tpy)Os(ttp)^{4+}$ and $Ru(ttp)_2^{2+}$ complexes, A was 1.9×10^{12} and 1.8×10^{12} s^{-1}, respectively, and ΔE was 1640 and 1600 cm^{-1}, respectively. This indicates that for both complexes and in the high temperature region, the lifetime of the Ru-based excited state is governed by a kinetically similar deactivation process which involves a MC state lying at practically the same energy level.

(iii) Low Temperature Behavior. For RuOs at $T < 200$ K, we ascribe the registered quenching of the Ru-based luminescence (Figure 1) to a Ru → Os energy transfer process. Evidence supporting this view comes from the observation that quenching of the Ru-based luminescence is accompanied by sensitization of the Os-based luminescence. Thus at 155 K (fluid solvent), irradiation of RuOs at $\lambda = 490$ nm, where a 1:1 excitation of the Ru- and Os-based chromophores is obtained, resulted in an higher Os-based luminescence intensity compared to the reference compound $Os(ttp)_2^{2+}$ (>50% sensitization). Likewise, from a previous study performed at 77 K in DMF/CH_2Cl_2 9:1 (frozen solvent), the Os-based time-resolved luminescence of RuOs exhibited a double exponential behavior, with a rise time (220 ns) that corresponded to the decay of the Ru-based luminescence.[9] Values for k_{en}, as calculated from eq 1, are plotted in Figure 1 (bottom panel). For RuOs, the critical temperature at which the Ru-based intrinsic deactivation and Ru → Os energy transfer rates are identical is $T_c = 184$ K.

In conclusion, we have found that the Ru → Os energy transfer rate in $(ttp)Ru(tpy\text{-}ph\text{-}bco\text{-}ph\text{-}tpy)Os(ttp)^{4+}$ is 5.2×10^6 s^{-1} (±20%) over the 200−90 K interval. Thus, energy transfer is neither affected by temperature changes nor by the state of the solvent, which is *fluid* at $T > 110$ K and *frozen* below that temperature.

The invariance of k_{en} may be understood in the frame of established models for electronic energy transfer, the exchange (Dexter)[16] and dipole−dipole (Förster)[17] approaches. According to the exchange mechanism, a very small temperature dependence is expected if energy transfer is activationless, $-\Delta G° = \lambda$, where λ is the reorganization energy.[3] In fact, in the present case, estimates give $\Delta G° = -0.26$ eV[11] and $\lambda = 0.2$ eV.[18] This suggests that Ru → Os energy transfer in RuOs occurs in the nearly activationless regime. According to the dipole−dipole mechanism, the energy transfer rate can be calculated from spectroscopic properties of the donor and the acceptor. We have found that the spectral overlap integral[17] between the emission spectrum of the donor and the absorption spectrum of the acceptor (on an energy scale) practically does not change with temperature, being 9.7×10^{-14} and 1.0×10^{-13} $cm^3\ M^{-1}$ at room temperature and 77 K, respectively.[19] Thus, the estimates made show that the observed independence of the energy transfer rate on temperature (Figure 1) is consistent with both the exchange and dipole−dipole mechanistic models.

Acknowledgment. We thank M. Minghetti and L. Ventura for technical assistance. This work was supported by the Progetto Strategico Tecnologie Chimiche Innovative of CNR, Italy. L.H. acknowledges personal grants from The European Commission (TMR Contract no. ERBFMBICT950352) and The Foundation Blanzeflor Ludovisi-Boncompagni, née Bildt.

JA962333V

---

[13] (a) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193. (b) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85. (c) Coe, B. J.; Thompson, D. W.; Culbertson, C. T.; Schoonover, J. R.; Meyer, T. J. *Inorg. Chem.* **1995**, *34*, 3385. (d) Maestri, M.; Armaroli, N.; Balzani, V.; Constable, E. C.; Cargill Thompson, A. M. W. *Inorg. Chem.* **1995**, *34*, 2759.

[14] The luminescent level of the related $Ru(bpy)_3^{2+}$ complex comprises a cluster of sublevels within an energy spacing of about 100 cm^{-1} that kinetically behaves as a single level for $T > 77$ K.[13]

[15] Barigelletti, F.; Belser, P.; von Zelewsky, A.; Juris, A.; Balzani, V. *J. Phys. Chem.* **1985**, *89*, 3680.

[16] Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 838.

[17] Förster, Th. *Discuss. Faraday Soc.* **1959**, *27*, 7.

[18] Obtained from the Stokes shift ($SS = 2\lambda^{Os}$) exhibited by $Os(ttp)_2^{2+}$, whose ground state to lowest triplet state absorption can be directly measured[8] and by assuming that $\lambda^{Ru} \approx \lambda^{Os}$, and $\lambda = \lambda^{Ru} + \lambda^{Os}$.

[19] (a) Within the dipole−dipole description of energy transfer, one should take into account the change of the refractive index of the solvent (n) on passing from fluid to frozen medium. From empirical expressions (ref 19b), one may estimate that n increases by approximately 20%, which would give the expected reduction of k_{en} by a factor of 2 (k_{en} is proportional to $1/n^4$, ref 17). However, in the dipole−dipole model, the solvent enters as a dielectric continuum, while in the present case a large part of the intercromophoric space is occupied by the bridging ligand. Thus, since the predicted reduction in k_{en} is relatively small and uncertain, the observed independence of k_{en} on the state of the solvent cannot be used as an argument against the Förster mechanism. (b) Mantulin, W. W.; Huber, J. R. *Photochem. Photobiol.* **1973**, *17*, 139.