

Table III. Equilibrium Composition at 24.6 °C and Order of Stability

isomer	mol %	ΔG° ^a	ΔH° ^b
myo	44.7		2.30
chiro	28.2	1.14	3.44
scyllo	18.8	2.14	
muco	5.7	5.10	7.40
(neo)	2.6	not calcd	not calcd

^a Referred to myo. ^b Calculated from ΔG° , taking into account entropic contributions from symmetry number and mixing of enantiomers. Values referred to scyllo.

The high reactivity of the cis isomer calls for two last observations. The conformational inversion **19** makes the hydrogens equivalent, and all can assume the highly reactive axial position (H_a); furthermore the accessibility of the reagents to the carbon atoms of the ring is very easy and attack on the face carrying axial hydrogens is favored. This fact greatly influences the reactivity of the cis compound, e.g., in H/D exchange.

During the epimerization of **3** in the presence of MeOD/MeONa, almost complete deuteration occurs before epimerization. GC-MS analysis of a mixture 45:35:20 of the cis, epi, and muco isomers (obtained after a short reaction time) shows that the starting compound cis contains about 70% d_6 and 30% d_5 molecules. We interpreted the phenomenon as an attack of the base onto a hydrogen H_a from the less-hindered side, further reaction with the solvent, and incorporation of H or D from the same side. All the steps of this process are very rapid. This stereochemical result is in contrast with our observations of the epimerization of the bicyclooctene esters **12-15**,²⁶ where deuterium incorporation coincides with epimerization. The difference between the two systems is in the lower reactivity of the bicyclooctenes, where no axial relationships exist between the hydrogen atoms and the adjacent COOR groups and in the lower difference in steric hindrance. Thus, a concerted mechanism is operating in which the addition of H^+ or D^+ occurs on the side opposite that undergoing attack of the base, with contemporary inversion of the configuration of the carbon.

During the heating of *cis*-cyclohexanhexacarboxylic acid (**3i**) in D_2O , we observed the same effect in the course of the NMR study of the chair inversion.³³ Around coalescence temperature, the cis acid signals broaden until they disappear. Under such conditions, the progressive appearance of a new compound could be detected. Its methine protons give rise to a five spin spectrum (a doublet of area 2 and two triplets of areas 1 and 2) that was attributed to the formation of the epi acid **4i** monodeuterated in position 6. When cooled, to room temperature, the spectrum of the nonepimerized cis acid **3i** shows no evidence of deuteration. Deuteration and epimerization come at the same stage of the reaction as was found for the bicyclooctenes. The contrast with alkaline epimerization discussed earlier prompted us to examine the epimerization of the **3h** ester under acid conditions. Studies are in progress and will be reported in the future.

The composition of the equilibrium mixture and the ΔG° values of the various isomers are reported in Table III. The most abundant isomer is myo with an axial substituent and not scyllo which is fully equatorial. Although rather strange at first sight, this datum is not unexpected, having been already observed for the hexamethylcyclohexanes.¹⁰

Taking into account the strong entropic destabilization of scyllo, owing to its high symmetry, and making the corresponding correction on ΔG° , the order of stability is scyllo, myo, chiro, muco, expressed as increasing values of the conformation energy.

The same conclusion can be reached from the data obtained in the epimerization of the hexamethylcyclohexanes on Pt/C at 250 °C. The equilibrium composition myo chiro scyllo is equal to 54:21:18 (plus other isomers). The value of ΔG° with reference to myo is 4.1 kJ mol⁻¹ for chiro and 4.8 kJ for scyllo. Correction with the symmetry factor gives a value for scyllo of -3.0 kJ mol⁻¹, in excellent agreement with that found in this paper.

Acknowledgment. This work was partly supported by a grant of Consiglio Nazionale delle Ricerche (CNR), Rome, Italy.

Registry No. **3h**, 77117-51-2; **3i**, 2216-84-4; **4h**, 94054-00-9; **6h**, 83861-33-0; **7h**, 83238-59-9; **9h**, 94054-01-0; **10h**, 94054-02-1; **11**, 1719-83-1; **12**, 56745-93-8; **13**, 56782-33-3; **14**, 56782-36-6; **15**, 56782-35-5.

Long Range Photoinduced Electron Transfer in a Rigid Polymer

Tom Guarr, Mark E. McGuire, and George McLendon*

Contribution from the Department of Chemistry, University of Rochester, River Station, Rochester, New York 14627. Received February 20, 1985

Abstract: Electron (hole) tunnelling reactions are studied in a rigid polymer medium by following the reductive quenching of a series of $Ru(LL)_3^{2+}$ homologues by a series of aromatic amines. Tunnelling distances up to 12 Å (edge to edge) are observed. The experimental data include a determination of the exponential damping factor α in the electronic term (H_{ab}). The data are consistent with a weak dependence of α on binding energy. Such a weak dependence is more consistent with a superexchange description than with a barrier tunnelling description of electron (hole) transfer. These reactions are shown to be essentially temperature independent between 298 K and 359 K, but are significantly slower at 77 K.

Although long distance electron transfer is central to biological systems^{1a} and to attempts to mimic such systems,^{1b} understanding of the parameters which control long distance (nonadiabatic) electron transfer is incomplete at best. Recently, data have become available from pulse radiolysis,² and photochemical studies³ which

may provide tests of the theoretical models¹ for long distance electron transfer.

In previous papers from this lab, reactions of $Ru(LL)_3^{2+}$ with MV²⁺ (methyl viologen) in glycerol were described.^{3a,b,4} Two

(1) (a) Chance, B.; Devault D.; Frauenfelder, H.; Marcus, R.; Schieffer, J.; Sutin, N. Eds.; "Tunnelling in Biological Systems"; Academic Press: New York, 1979. (b) Devault, D. *Q. Rev. Biophys.* **1980**, *13*, 387-564. (c) Sutin, N. *Acc. Chem. Res.* **1982**, *15* 275-282. (d) Guarr, T.; McLendon, G. *Coord. Chem. Rev.*, to be published.

(2) (a) Miller, J. R. *Science* **1974**, *189*, 221-222. (b) Beitz, J. V.; Miller, J. R. *J. Chem. Phys.* **1979**, *71*, 4579-4595.

(3) (a) Guarr, T.; McGuire, M.; McLendon, G.; Strauch, S. *J. Am. Chem. Soc.* **1983**, *105*, 616-618. (b) Strauch, S.; Guarr, T.; McGuire, M.; McLendon, G. *J. Phys. Chem.* **1983**, *87*, 3579-3581. (c) Miller, J. R.; Peoples, J. A.; Schmitt, M. J.; Closs, G. L. *J. Am. Chem. Soc.* **1982**, *104*, 6488-6493. (d) Miller, J. R.; Hartman, K. N.; Abrash, S. *J. Am. Chem. Soc.* **1982**, *104*, 4296-4298. (e) Namiki, A.; Nakashima, N.; Yoshihara, Y. *J. Chem. Phys.* **1979**, *71*, 925-930.

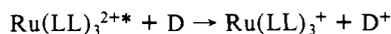
(4) McGuire, M. E.; McLendon, G. *J. Phys. Chem.*, submitted.

problems were inherent in these studies.

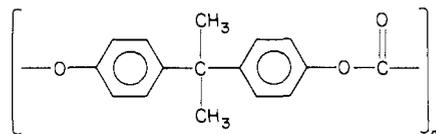
First, since the high-concentration species (MV^{2+}) is charged, a nonrandom distribution of molecules results. In principle, this can be accounted for by the use of an appropriate distribution function. However, such distribution functions commonly assume point charges and are not valid at the high concentrations necessary for our measurements. Secondly, some complications from diffusional motion can occur for the longer lived excited states. The use of very short lived species to circumvent this problem is precluded by the need for electron transfer to complete with normal decay channels in order to be observed.

Finally, recent experiments indicate that the rate of electron transfer in these types of systems is controlled by the dielectric relaxation time of the solvent.^{4,5} Evidence now exists that the reorganization energy, E , and/or ΔE , may become time dependent when solvent reorganization is slow.^{4,5} This leads, of course, to a dispersion of ET rates. Therefore, analysis of data in systems with slow solvent dielectric relaxation rates will be complicated by uncertainty in important parameters. For example, studies of the temperature dependence of ET rate in such systems will yield data due, at least in part, to the temperature dependence of the dielectric relaxation rate.

The present work describes studies of the ET reactions



where D is an organic reductant. The medium is a polymeric film with the structure



It is commonly referred to as a polycarbonate or polydian (or by the trademark "Lexan"). Both the mechanical and dielectric properties of this material have been well studied.⁶

Many of the problems encountered in the glycerol experiments are avoided in this system. For example, since D is uncharged, its distribution in the polymer matrix is expected to be randomized. Secondly, the diffusion of reactants is negligible on the time scale of electron transfer ($\sim 2 \mu s$).

In addition, this system better lends itself to the study of the dependence of rate on exothermicity. No donor-acceptor adduct formation is observed between $Ru(LL)_3^{2+}$ homologues and the organic reductants in the polymer matrix. Further, ruthenium complexes are available that push the reaction driving force to ~ 1.2 V (measured in CH_2Cl_2).

Polycarbonate was chosen as the matrix material for several reasons. First, the technology for making polycarbonate films is readily available and easily mastered. Thus, a wealth of data corresponding the properties of this material exists.⁶ Secondly, the polymer, reductants, and Ru complexes are all soluble in CH_2Cl_2 . A final advantage concerns the effect of temperature on the dielectric relaxation rate in this particular material. In polycarbonate, there are two dielectric relaxation processes. While the α relaxation is very slow at room temperature, the β relaxation occurs in $<10^{-6}$ s at 25 °C and $<10^{-7}$ s at 80 °C. Therefore, for measurement of ET rates up to $\sim 10^6$ s⁻¹, a convenient "temperature window" of ~ 20 to ~ 100 °C is available⁶ where the dielectric relaxation rate is expected to be relatively constant. Thus, through studies of collisionless electron transfer in Lexan, the following specific questions can be addressed: (1) How does electron transfer rate $k_{et}(R)$ depend on donor-acceptor distance, R ? (2) How does $k_{et}(R)$ depend on reaction exothermicity? (3)

How does $k_{et}(R)$ depend on temperature? (4) How does $k_{et}(R)$ depend on electron (or hole) binding energy?

Materials and Methods

Materials. $RuCl_3 \cdot H_2O$ (Aldrich) was used without further purification. 1,10-phenanthroline (abbreviated phen), 5-chloro-1,10-phenanthroline (5-Cl-phen), 4,7-dimethyl-1,10-phenanthroline (4,7-Me₂phN or Me₂phen), 2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine (Me₂bpy), and 3,4,7,8-tetramethyl-1,10-phenanthroline (Me₄phen) were obtained from G. Frederick Smith Co. and were used as received.

Preparation of 4,4'-(COOC(CH₃)₂)₂bpy (Abbreviated ester). This ligand was prepared according to the method of Delaive et al.⁷

Preparation of $Ru(LL)_2Cl_2$ (Except $Ru(4,4'-(COOC(CH_3)_2)_2bpy)_2Cl_2$). These compounds were prepared according to the method of Sprintschnik et al.¹¹

Preparation of $Ru(LL)_3^{2+}$ Complexes (Except $Ru((4,4'-(COOC(CH_3)_2)_2bpy)_3^{2+})$. These were generally prepared from the corresponding $Ru(LL)_2Cl_2$ by refluxing with excess ligand for a few hours in methanol. Isolation of the product involved addition of water, followed by addition of aqueous $NaClO_4$ or $LiCl$ and filtration.

Alternatively, these compounds could be prepared by the method of Lin et al.⁸

Preparation of $Ru(4,4'-(COOC(CH_3)_2)_2bpy)_3^{2+}$ (Abbreviated $Ru(ester)_3^{2+}$). This compound was synthesized by the procedure of Delaive et al.⁷ The complex could be purified by gel filtration (Sephadex LH-20; 1:1 methanol/acetone). However, a simpler method was to simply wash the crude product with several small portions of methanol. (Although the product was somewhat soluble in methanol, the impurities were soluble to a much greater extent.) Analysis of a sample treated in this manner gave the following: Anal. Found (calcd); C, 46.94 (47.13); H, 4.47 (4.36); N, 6.01 (6.11). The visible spectrum was very similar to that of other $Ru(LL)_3^{2+}$ complexes, with $\gamma_{max} = 464$ nm in acetone.

Preparation of $Ru(4,4'-(COOC(CH_3)_2)_2bpy)_2(bpy)^{2+}$ (Abbreviated $Ru(ester)_2^+(bpy)^{2+}$). The bis(ester) complex was prepared by refluxing the $Ru(4,4'-(COOC(CH_3)_2)_2bpy)_2Cl_2$ (obtained in the above $Ru(ester)_3^{2+}$ preparation) with a stoichiometric amount of bipyridine in 2-propanol for 3.5 days. Isolation was carried out in the same way as for the tris(ester) complex above. Anal. Found (calcd) C, 45.81 (45.88); H, 4.19 (3.99); N, 6.89 (6.98).

The visible spectrum revealed a slightly broader peak than that found for the tris(ester), with $\lambda_{max} = 473$ nm (acetone).

Preparation of $Ru(4,4'-(COOC(CH_3)_2)_2bpy)(bpy)^{2+}$ (Abbreviated $Ru(bpy)_2(ester)^{2+}$). The mono(ester) complex was prepared by refluxing a stoichiometric amount of 4,4'-(COOC(CH₃)₂)₂bpy with $Ru(bpy)_2Cl_2$ in 2-propanol for 1.5 days. The isolation procedure was identical with that for the tris(ester) complex. The major peak in the visible was very broad and centered at ~ 472 nm (acetone). For this complex, the high energy shoulder normally present in $Ru(LL)_3^{2+}$ spectra was much more pronounced.

Purification of Organic Reductants. *N,N,N',N'*-Tetramethyl-*p*-phenylenediamine (abbreviated TMPD) was obtained from Aldrich and was purified by twofold vacuum sublimation, then carefully dried on a vacuum line. *N,N,N',N'*-Tetramethylbenzidine (TMB, Aldrich), 10-methylphenothiazine (10-MP, Eastman), triphenylamine (Ph₃N, Aldrich), and *N,N*-dimethyl-*p*-chloroaniline (*p*-CDMA, Overlook Industries) were also purified by vacuum sublimation.

N,N-Dimethyl-*p*-toluidine (DMT, Aldrich) was distilled over BaO (Fisher) and stored over KOH (Baker).

N,N-Dimethyl-*p*-methoxyaniline (*p*-MDMA) was prepared⁹ by the following procedure: First 18.5 g (0.15 mol) of *p*-anisidine (Aldrich, purified by vacuum sublimation) was suspended in ~ 300 mL of cold H_2O (0–5 °C) and to this was added 39 g (0.46 mol) of $NaHCO_3$ (Baker). Slowly, with stirring, 0.38 mol (~ 36 mL) of dimethyl sulfate was added carefully in small increments, and the mixture was kept at ~ 10 °C. When the CO_2 evolution stopped or appeared controlled, the solution was allowed to come to room temperature and kept stirring at 20–25 °C for 0.5 h. (The mixture must be above 18 °C to hydrolyze excess dimethyl sulfate). A white solid was then filtered out of the mixture, dried briefly under vacuum (aspirator), and then vacuum sublimed twice. White crystals were obtained, mp 44–47 °C (lit. mp 43 °C).⁹

The purity of the organic reductants was checked by NMR.

(5) (a) Miller, J. R.; Beitz, J. V.; Huddleston, R. K. *J. Am. Chem. Soc.* **1984**, *106*, 5057–5068. (b) Van Duyne, R. P.; Fischer, S. F. *Chem. Phys.* **1974**, *5*, 183–197. (c) Duke, C. B.; Meyer, R. *J. Phys. Rev. B: Condens. Matter* **1981**, *23*, 2111–2125.

(6) (a) McCrum, N. G.; Read, B. E.; Williams, G. In "Anelastic and Dielectric Effects in Polymeric Solids"; Wiley and Sons: London, 1967. (b) Schnell, H. *Agnew. Chem.* **1956**, *68*, 633–640. (c) Christopher, W. F.; Fox, D. W. In "Polycarbonates"; Reinhold: New York, 1962.

(7) DeLaive, P. J.; Lee, J. T.; Abruna, H.; Sprintschnik, H. W.; Meyer, T. J.; Whitten, D. G. *Adv. Chem. Ser.* **1978**, *No. 168*, 28–43.

(8) Lin, C. T.; Bottcher, W.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6536–6544.

(9) (a) Mangini, A.; Passerini, R. *J. Chem. Soc.* **1956**, 4954–4959. (b) Sekiya, M.; Tomie, M.; Leonard, N. J. *J. Org. Chem.* **1968**, *33*, 318–322.

Spectral grade methylene chloride (Mallinckrodt) was used as received in most cases. In experiments involving the bipyridyl ester complexes, the methylene chloride was distilled over CaSO_4 several times, and then dried over molecular sieves. This was done in order to prevent complications due to impurities for these easily reduced ruthenium complexes. 2-Propanol (Baker) and 1,4-dioxane (Mallinckrodt, AR) were used as received.

Polycarbonate resin was purchased from Scientific Polymer Products and was used as received.

Electromagnetic grade tetrabutylammonium fluorophosphate, or tetrabutylammonium bromide were purchased from Southwestern Analytical and used as received.

Water was deionized and glass distilled.

Methods

IR spectra were recorded on a Perkin Elmer Model 467 infrared spectrophotometer. Visible and UV spectra were obtained on either a Cary 118, a Perkin Elmer Lambda-3, or a Perkin Elmer 330. NMR spectra were obtained on a Varian 90-MHz or Nicolet 300-MHz instrument.

Electrochemical data were collected on a Princeton Applied Research Model 173 potentiostat in conjunction with a Model 175 universal programmer. The reference electrode was either a SCE (PAR) or a Ag/AgCl electrode (Bio-Rad). The working electrodes used were either Au, Pt, or glassy carbon electrodes supplied by BAS and were freshly polished before each use. The auxiliary electrodes were Pt.

Static emission measurements were made in a Perkin-Elmer MPF-44A spectrofluorimeter. Experiments from 20–80 °C were performed with use of a solid sample holder accessory, and measurements at 77 K were done in an optical dewar kindly supplied by R. Eisenberg.

Lifetimes were measured with use of the second harmonic of a Quanta-Ray DCR-2 Nd:YAG laser excitation source. Emission was detected at 90° by a 1P28 photomultiplier tube coupled to a Biomation 6500 transient digitizer. The system was interfaced to a Digital LSI-II/03 computer.

The Lexan films were prepared by spreading a solution of 10:1 (w/w) methylene chloride–polycarbonate on a carefully cleaned glass plate with use of doctor blade technique. The CH_2Cl_2 evaporated rapidly, leaving a polycarbonate film of a reproducible thickness. Average film thickness was roughly $12 \pm 3 \mu\text{m}$, as measured by a high-precision micrometer.

A typical experiment was as follows: Two stock solutions were made. One contained CH_2Cl_2 , polycarbonate (10:1, w/w), and the desired ruthenium complex. The second contained an additional component, a known amount of organic reductant, D. (This stock solution was ~0.01 to 0.1 M in D, depending on the experiment.) By mixing of the two stocks, solutions with various concentrations of D could be made. This mixing and the actual pouring of the films were carried out in the dark, to eliminate the possibility of the photoinduced electron-transfer reaction occurring in solution.

No complications from photochemistry would have arisen if the reaction were reversible and the back-reaction fast. However, one of these conditions is not met, as demonstrated qualitatively by shining a light on a solution containing a ruthenium complex and TMPD. After a short time (which was dependent on the particular ruthenium complex), the solution turned from yellow–orange to a very dark green or blue. Two new bands in the visible, at 560 and 615 nm, corresponded to the one electron oxidation product,¹⁰ TMPD^+ . After a period of minutes to hours, the yellow–orange color returned. However, cycling several times produced a noticeable darkening of the solution, indicative of net TMPD^+ formation. Such a situation would occur if some of the $\text{Ru}(\text{LL})_3^+$ transient reacted with impurities or another solution species (other than TMPD^+) producing $\text{Ru}(\text{LL})_3^{2+}$. Some darkening of the TMPD -containing solutions prior to film pouring was observed for several of the ruthenium complexes, but it did not appear to be severe. In the worst case, the concentration buildup of TMPD^+ amounted to only 1–2% of the total TMPD present. Furthermore, this darkening was largely prevented by rigorous purification and drying of the CH_2Cl_2 .

The films were poured on clean glass strips, about 4 cm × 20 cm, and were either air or vacuum dried overnight in the dark. The concentration of D in each dried film was linearly related to the solution concentration by a factor of 9.1. In other words, a 10:1 CH_2Cl_2 /polycarbonate solution 0.010 M in D produced a dried film which was 0.091 M in D. The emission intensity was measured at 5 points in each film and the values averaged. No emission was observed from a blank film containing no ruthenium.

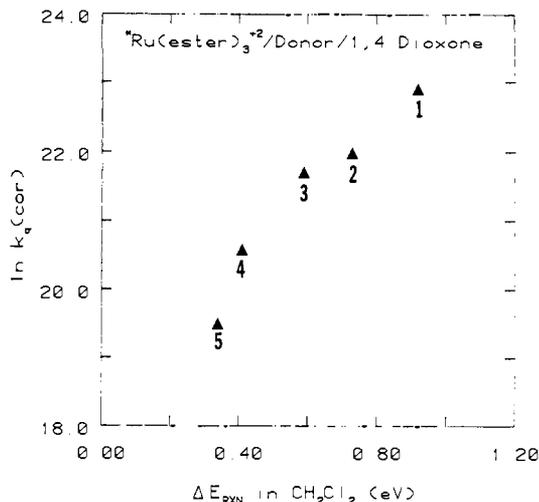


Figure 1. Plot of k_q ($\text{M}^{-1} \text{s}^{-1}$) (corrected for diffusion) vs. ΔE_{rxn} values for the reactions of $\text{Ru}(\text{ester})_3^{2+}$ with TMB (1), *p*-MDMA (2), DMT (3), *p*-cDMA (4), and Ph_3M (5). ΔE_{rxn} values are from Table I. All reactions are in neat 1,4-dioxane at room temperature and air equilibrated.

The experiments in neat 1,4-dioxane were carried out by measuring the fluorescence quenching of $\text{Ru}(\text{ester})_3^{2+}$ by various concentrations of the appropriate organic reductants D. The solutions were air equilibrated. K_{SV} values were determined by the usual Stern–Volmer quenching plots. The reactions were carried out at room temperature. The observed k_q values were corrected for diffusion effects in the following manner. The diffusion-corrected k_q values, $k_q(\text{cor})$ can be calculated as^{12a}

$$1/k_q(\text{cor}) = 1/k_q(\text{obsd}) - 1/k_D$$

Here, k_D is the calculated diffusion controlled rate constant, which is calculated to be $\approx 8.5 (\pm 1.0) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, using the Smoluchowski equation.³⁰

Results and Discussion

Electrochemistry and Reaction Thermodynamics. Redox potentials of all the ruthenium complexes and organic reductants were measured at room temperature in dichloromethane (Table I). The low dielectric of polycarbonate ($\epsilon = 2.6$) will cause a shift of these potentials due to the change in solvation energy. In principle, this shift could be estimated by using the Born equation. In practice, the shift can be empirically derived by monitoring collisional photoinduced ET rates in a low dielectric medium similar to polycarbonate (e.g., dioxane, $\epsilon \approx 2.20$).

Whitten et al.^{12a} and Ballardini et al.^{12b} have shown that the rate of diffusional ET quenching of excited states by aromatic amines is diffusion controlled when $\Delta E \geq 0.5 \text{ V}$, but decreases sharply (by 10–100×) when $\Delta E < 0 \text{ V}$. Thus the “break” in the ΔE vs. rate curve is a good empirical estimation of $\Delta E = 0 (\pm 0.1) \text{ V}$ for a reaction series in a particular medium. Subsequently, several of the reactions studied in Lexan have been monitored in 1,4-dioxane (Figure 1) and their rates plotted vs. the measured ΔE_{rxn} from electrochemical data in CH_2Cl_2 . As can be seen from Figure 1, k_q (corrected for diffusion effects) drops off to an order of magnitude below k_D at $\Delta E_{\text{rxn}} \approx 0.3 \text{ V}$ (in CH_2Cl_2). Using this empirical approximation, we conclude that the actual reaction exothermicities of our reactions in Lexan, ΔE_{cor} , are $\sim 0.3 (\pm 0.1) \text{ V}$ less favorable than we would calculate from $E_{1/2}$ values in CH_2Cl_2 . This assumes that effects of ion-pairing (vide infra) are similar in Lexan ($\epsilon = 2.6$) and 1,4-dioxane ($\epsilon = 2.20$). ΔE_{rxn} and ΔE_{cor} values are listed in Table I. Rigorously, the point at which k_q noticeably decreases depends on the total reorganization energy E_r , which varies from solvent to solvent. However, even if E_r were estimated to be as low as $\sim 0.25 \text{ eV}$, the above procedure would

(10) Michaelis, L.; Schubert, M. P.; Granick, S. *J. Am. Chem. Soc.* **1939**, *61*, 1981–1992.

(11) Sprintschnik, G.; Sprintschnik, H. W.; Kirsch, P. P.; Whitten, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 4947–4954.

(12) (a) Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4815–4824. (b) Ballardini, R.; Varani, G.; Indelli, M. T.; Scandola, F.; Balzani, V. *J. Am. Chem. Soc.* **1978**, *100*, 7219–7223.

Table I

electron donor ^a /electron acceptor ^b		ΔE_{rxn} , ^e V	ΔE_{cor} , ^h V	R_c^{obsd} , ⁱ Å	$\tau_0(\text{Ru})$, ^j μs	$R_c^{\tau,k}$ Å	$R_c^{\text{cor},q}$ Å
$E_{1/2}(1+/0)$, ^{c,f} V	$E_{1/2}(2+/1+)$, ^{c,d} V						
TMPD/0.46	Ru(Me ₄ phen) ₃ ²⁺ /~-1.33 ^e	~0.31	~0.01	10.2	3.7 ^m	8.9	10.2
TMPD/0.46	Ru(Me ₂ phen) ₃ ²⁺ /~-1.21 ^e	~0.43	~0.13	11.7	3.3 ^m	10.5	11.4
TMPD/0.46	Ru(phen) ₃ ²⁺ /-1.01	0.13	~0.33	13.7	2.5 ^m	12.8	13.5
TMPD/0.46	Ru(5-Clphen) ₃ ²⁺ /-0.85	0.79	~0.49	15.8	2.8 ^m	14.8	15.3
TMPD/0.46	Ru(ester)(bpy) ₂ ²⁺ /-0.55	1.09	~0.79	16.2	2.4 ^{m,n}	15.3	15.8
TMPD/0.46	Ru(ester) ₂ (bpy) ²⁺ /-0.48	1.16	~0.86	19.0	2.24 ⁿ	18.2	18.5
TMPD/0.46	Ru(ester) ₃ ²⁺ /-0.46	1.18	~0.88	19.6 ^p	2.21 ⁿ	18.8	19.1
TMB/0.72	Ru(ester) ₃ ²⁺ /-0.46	0.92	~0.62	19.4	2.21 ⁿ	18.6	19.3 ^r
<i>p</i> -MDMA/0.91	Ru(ester) ₃ ²⁺ /-0.46	0.73	~0.43	16.1 ^p	2.21 ⁿ	15.3	15.8
DMT/1.05	Ru(ester) ₃ ²⁺ /-0.46	0.59	~0.29	13.1	2.1u ⁿ	12.3	13.0
10-MP/1.07	Ru(ester) ₃ ²⁺ /-0.46	0.57	~0.27	13.1	2.21 ⁿ	12.3	13.0
<i>p</i> -CDMA/1.23	Ru(ester) ₃ ²⁺ /-0.46	0.41	~0.11	10.4	2.21 ⁿ	9.6	10.7
Ph ₃ N/1.29	Ru(ester) ₃ ²⁺ /-0.46	0.35	~0.05	7.3	2.21 ⁿ	6.5	8.5

^aTMPD = *N,N,N',N'*-tetramethyl-*p*-phenylenediamine; TMB = *N,N,N',N'*-tetramethylbenzidine; *p*-MDMA = *p*-methoxydimethylaniline; DMT = dimethyl-*p*-toluidine; 10-MP = 10-methylphenothiazine; *p*-CDMA = *p*-chlorodimethylaniline; Ph₃N = triphenylamine. ^bRu(LL)₃²⁺; (LL): Me₄phen = 3,4,7,8-tetramethylphenanthroline; Me₂phen = 4,7-dimethylphenanthroline; phen = phenanthroline; 5-Clphen = 5-chlorophenanthroline; bpy = 2,2'-bipyridine; ester = 4,4'-diisopropyl ester 2,2'-bipyridine. ^cReduction potentials vs. NHE (room temperature). ^dMeasured in CH₂Cl₂, 0.1 M tetra(*n*-butyl)ammonium bromide, using a glassy carbon electrode and a Ag/AgCl reference electrode. 0.208 V has been added to the experimental values to convert to values vs. NHE. ^eThese values are estimates due to the irreversibility exhibited by these complexes. ^fMeasured in CH₂Cl₂, 0.1 M tetra(*n*-butyl) ammonium fluorophosphate with a Au electrode and a SCE reference electrode. Values converted to NHE by adding 0.242 V to measured $E_{1/2}$. ^g ΔE_{rxn} values for the reaction Ru(LL)₃²⁺ + donor \rightleftharpoons Ru(LL)₃⁺ + donor⁺ have been obtained by the relation

$$E^* + E_{1/2}(\text{Ru}(\text{LL})_3^{2+/1+}) - E_{1/2}(\text{donor}^{+/0}) = \Delta E_{\text{rxn}}$$

E^* has been taken as 2.10 V for all complexes.^{7,24} ^h ΔE_{rxn} values that have been empirically corrected for the potential shift caused by the polycarbonate medium from the results of diffusional electron transfer experiments in dioxane (see text for details). It is assumed that the polarization energies of the various Ru complexes are equal, and that the polarization energies of the various aromatic electron donors are similar. Reflecting the assumptions in this correction, an uncertainty of ± 0.1 V is assigned to the ΔE_{cor} values. ⁱCritical distance (room temperature) calculated with the Perrin formulation (eq 4). ^kCritical distance corrected to $\tau_0 = 1$ μs with eq 5. ^lRadiative lifetimes (μs) of Ru complexes measured in Lexan at room temperature. ^mSlow component of radiative decay in Lexan. ⁿDecay nearly exponential. ^pAverage of two determinations. ^q R_c^{cor} corrected for the finite volume of the reactants. See eq 6 in text. $R_f \approx 7 \pm 1$ Å. $R_0 \approx 9 \pm 1$ Å for reactions with TMB.

Table II

reactant pair	ΔE_{cor}^a , V	$R_c^{\tau}(298\text{K})$, Å ^b	$R_c^{\tau}(77\text{K})$, Å ^b	Δ rate ^c
*Ru(ester) ₃ ²⁺ /TMPD	0.88	18.9 (± 0.15)	15.9 ($\begin{smallmatrix} +0.2 \\ -0.9 \end{smallmatrix}$)	~18
*Ru(5-Clphen) ₃ ²⁺ /TMPD	0.49	14.6 (± 0.8)	10.5 ($\begin{smallmatrix} +0.7 \\ -0.9 \end{smallmatrix}$)	~70
*Ru(Me ₂ phen) ₃ ²⁺ /TMPD	0.13	10.6 (± 0.3)	6.4 ($\begin{smallmatrix} +0.5 \\ -1.1 \end{smallmatrix}$)	~61

^a ΔE_{rxn} (in CH₂Cl₂) -0.3 V = ΔE_{cor} (see text). ^b R_c^{obsd} corrected to 1 μs τ_0 assuming $\alpha \approx 0.5$ for all reactions. Luminescence lifetimes τ_0 at room temperature are listed in Table I for these Ru complexes. At 77 K, $\tau_0 = 5.4, 10.7, 11.0$ μs resp. for Ru(ester)₃²⁺, Ru(5-Clphen)₃²⁺, and Ru(Me₂phen)₃²⁺. The above reported R_c^{τ} values are not corrected for molecular volumes as are the R_c^{cor} values in Table I. The reason for this is that at low R_c^{τ} values, correcting for R_0 becomes an inaccurate correction, since it obscures rate differences between reactions with $R_c^{\tau} < 7$ Å. Therefore, we believe that in this system the R_c^{τ} values, corrected only for τ_0 , give a better estimation of rate differences at two different temperatures. ^cEstimated change in rate (at $R = \sim 12.5$ Å) between room temperature and 77 K using R_c^{obsd} values, $\alpha \approx 0.5$, and appropriate τ_0 values described by Miller^{2a}.

be valid. Assuming $E_r = 0.25$ eV, $k_q(\Delta E = 0) \approx 5 \times 10^{10}$ M⁻¹ s⁻¹ for the Ru(ester)₃²⁺/TMPD couple.²⁹ Nevertheless $k_q(\Delta E = -0.1) = 0-1.4 \times 10^8$ M⁻¹ s⁻¹, a full order of magnitude below k_p . Therefore, within the quoted experimental error, the method of ΔE estimation is valid.

It is assumed that the differences in ΔE ($\Delta\Delta E$) for the reactions in Lexan or dioxane and CH₂Cl₂ are relatively constant. This trend seems to generally be true for the organic reductants, with the reduction potential shifting quite consistently (~ 0.1 V) from CH₃CN to CH₂Cl₂. TMB seems to only shift by about 50 mV, but its larger size probably provides a smaller polarization energy than the other TMPD homologues. Ph₃N, whose $E_{1/2}$ does not seem to shift at all from CH₃CN to CH₂Cl₂, seems to be a special case in this series of organic reductants. The homologous series of Ru complexes are assumed to have similar polarization energies and thus similar shifts in $E_{1/2}$ values upon changing the medium dielectric.

It is noteworthy that the empirical ΔE_{cor} values (Table I) so measured are significantly lower in dioxane compared to dichloromethane. If the ruthenium complexes are dissociated to give (RuL₃)²⁺ dications, a significant increase in ΔE would be

predicted in the lower dielectric medium. It is clear, therefore, that the (RuL₃)Cl₂ complexes must be strongly ion paired in dioxane and also in Lexan. The magnitude of the potential shift of the (RuL₃)Cl₂/D systems between CH₂Cl₂ and dioxane suggests that both Cl⁻ ions are strongly associated with RuL₃²⁺. The presence of such strong association raises the possibility of (RuL₃)_x aggregation. Such aggregation is not likely, based on two experiments.

First, emission measurements show RuL₃ emission intensity scales linearly with [RuL₃] concentration, and that RuL₃ lifetimes are unaffected by [RuL₃] concentration. Triplet quenching is known to occur when RuL₃ complexes are brought in close proximity.¹³ The lack of such quenching suggests (RuL₃)_x aggregation is minimal.

A second experiment (suggested by John Miller) supports the absence of significant (RuL₃)_x aggregation in low dielectric media. Quenching of the benzophenone triplet state by (tris(4,4'-dicarboxyethyl ester bipyridine)ruthenium(II))Cl₂ was studied in dioxane ($\epsilon = 2.0$) and in acetonitrile ($\epsilon = 38.8$). In acetonitrile, (RuL₃)Cl₂ is dissociated into free ions so that no aggregation occurs. Within experimental error the same (diffusion controlled) rate of triplet quenching was observed in both solvents at identical concentrations of ruthenium complexes. This result demonstrates that the number of quencher particles is identical within experimental error in dioxane and acetonitrile, obviating the possibility of significant aggregation.

Distance Dependent: Static Quenching Experiments. The rate of charge transfer (tunnelling) in a rigid medium is assumed to depend strongly and exponentially on distance.¹⁴⁻¹⁷

$$W_{\text{ET}} = C|H_{\text{ab}}|^2[FC] \quad (1)$$

where

$$|H_{\text{ab}}| = V_0 \exp(-\alpha R) \quad (2)$$

(13) Milosavljevic, B. H.; Thomas, J. K. *J. Phys. Chem.* **1983**, *87*, 616-621.

(14) Hopfield, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 3640-3644.

(15) Jortner, J. *J. Chem. Phys.* **1976**, *64*, 4860-4867.

(16) Kuznetsov, A. M.; Sondergard, N. C.; Ulstrup, J. *J. Chem. Phys.* **1978**, *29*, 383-390.

(17) Gamow, G. Z. *Phys.* **1928**, *51*, 204-212.

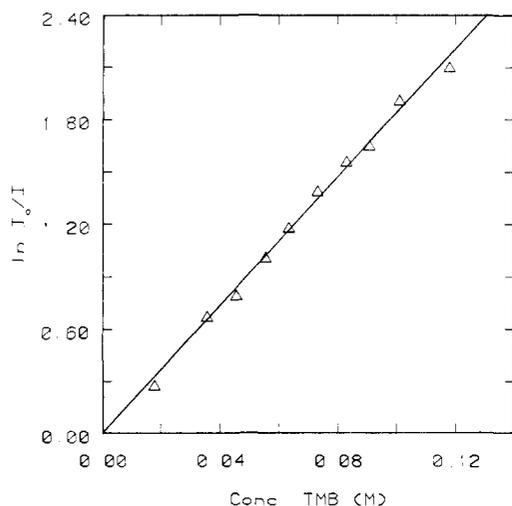


Figure 2. Typical Perrin plot (eq 4) for reaction in Lexan. Here is shown the reaction of $\text{Ru(ester)}_3\text{Cl}_2^*$ with TMB in Lexan at room temperature.

α = a damping factor, related to the tunnelling barrier height, R = the distance between localized electronic sites, C and V_0 are constants, [FC] represents a Franck-Condon term:^{5a}

$$\sum_{n=0}^{\infty} [(e^{-S} S^n / n!) \exp(-[(\Delta G^\circ + E_S + n\hbar\omega)^2 / (4E_S k_B T)])] \quad (3)$$

In equation 3 E_S = the medium reorganization energy (vide infra), $\hbar\omega$ = an average vibrational frequency for modes displaced by oxidation/reduction, ΔG° = the thermodynamic driving force, $S = E_c / \hbar\omega$ where S is the electronic coupling strength and E_c is the molecular reorganization energies of the donor/acceptor, k_B = the Boltzman constant, and T = the temperature.

The distance dependence of rate is contained in the electronic coupling matrix element, $|H_{ab}|$, which is predicted to decrease exponentially with increasing donor-acceptor separation distance.¹⁵ The dependence of the rate on thermodynamic driving force ΔG° , reorganization energy E_r , ($E_s + E_c$), and the temperature, T , all are contained in the FC term.

The rates of the general reactions



in rigid Lexan polymer can conveniently be described in terms of a "critical distance", R_c , for quenching of the excited state Ru(LL)_3^{2+*} by a random distribution of the neutral organic reductants D . R_c is derived by fitting the static fluorescence quenching data of the above reactions to the Perrin model.¹⁸ This model has been shown to accurately describe the fluorescence quenching of a luminescent probe by a random distribution of quenchers.

$$(I_0/I) = \exp(NV[Q]) \quad (4)$$

where, I_0 = the emission intensity in the absence of quencher, I = the observed emission intensity, N = Avogadro's number, $[Q]$ = the concentration of quencher, and V = the volume of a "quenching sphere".

Experimentally, the organic reductants D were seen to quench the luminescence of Ru(LL)_3^{2+*} complexes in polycarbonate films, and the data obtained fit well to eq 4 (see Figure 2). The excellent fit of the luminescence quenching data provides evidence for the total inhibition of diffusion in these systems. The mechanism of quenching is presumed to be electron transfer, as observed in solution.^{12a,b} Further evidence for an ET mechanism is the observation that the rate depends strongly on ΔE . This fact is inconsistent with alternative mechanisms such as energy transfer. No spectroscopic evidence for Ru(LL)_3^{2+*} - D association was observed in the Lexan polymer. Consequently, we postulate that quenching occurs solely by long-range electron transfer, and there

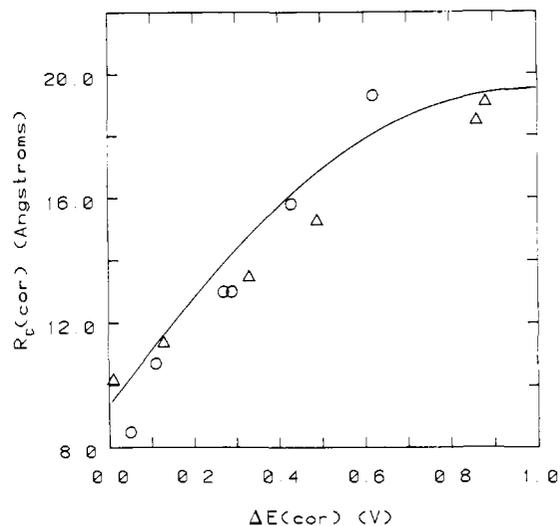


Figure 3. Plot of R_c^{cor} (Å) vs. ΔE_{cor} values for all reactions listed in Table I: (Δ) reactions with $\text{Ru(LL)}_3^{2+*}/\text{TMPD}$; (\circ) reactions with $\text{Ru(ester)}_3^{2+*}/\text{D}$. The solid line is fit to classical (Marcus) theory, assuming $E_r = 1.1$ V.

are no donor-acceptor association processes which lead to quenching. The critical distance R_c (Å) for various $\text{Ru(LL)}_3^{2+*}/\text{D}$ reactions is obtained by fitting the static quenching of Ru(LL)_3^{2+*} by various concentrations of D to the Perrin eq 4, as seen for one $\text{Ru(LL)}_3^{2+*}/\text{D}$ pair in Figure 2. From the slope of this plot, one obtains a "quenching volume", assumed spherical, around each Ru(LL)_3^{2+*} complex.^{3a} From this quenching volume, one obtains a "quenching radius" or "critical distance", R_c (Å), which is the distance at which the ET rate equals $1/\tau_0$, where τ_0 is the radiative lifetime of Ru(LL)_3^{2+*} . All distances R_c are assumed center to center, unless otherwise indicated.

From the data in Table I, it is seen that the experimentally observed R_c , R_c^{obsd} , generally increases with increasing reaction exothermicity. However, in order to accurately compare the critical distances at various ΔE values, two corrections to R_c^{obsd} must be made. First, a lifetime correction must be made which scales all reactions to the same luminescence decay time (τ_0). Equation 5^{3a,c} provides critical distances R_c^r , corrected to a τ_0 of 1 μs . Here, α is the experimentally determined damping factor

$$R_c^r = R_c^{\text{obsd}} + (2\alpha) \ln \tau_0 \quad (5)$$

(vide infra) and τ_0 is the luminescence lifetime of the Ru complex in μs . τ_0 and R_c^r values are listed in Table I.

A correction must also be made to the R_c^r values to account for the finite size of the reactants.^{3a,c}

$$(R_c^{\text{cor}})^3 = (R_c^r)^3 + (R_0)^3 \quad (6)$$

R_0 is the estimated sum of the radii of the reactants and is taken as $\sim 7 \pm 1$ Å, unless otherwise noted. R_c^{cor} values listed in Table I thus represent both lifetime and volume corrected critical distances. R_c^{cor} values are plotted vs. ΔE in Figure 3, and increase as predicted in eq 1-3. It can be noted that the magnitude of the R_c values for excited-state ET for $\text{Ru(LL)}_3^{2+*}/\text{D}$ in Lexan are appreciably larger than for the oxidative quenching of $\text{Ru}(\text{bpy})_3^{2+*}$ homologues by methyl viologen in rigid glycerol.^{3a} This is especially true when edge-to-edge distances are compared. R_{max} (edge-to-edge) in Lexan is ~ 12 Å at $\Delta E = 1$ V while in glycerol R_{max} (edge-to-edge) ~ 5 Å at a similar ΔE .

Time-Resolved Measurements. The actual dependence of ET rate on distance (e.g., the magnitude of H_{ab} , α , and thus the tunnelling barrier height, eq 2) cannot be obtained by calculations of R_c from static measurements. This is because the spread of donor-acceptor distances in a random matrix leads to a dispersion of ET rates. Rather, α , and thus barrier heights, must be determined from more difficult time-resolved emission measurements.

The decay of donor luminescence in the presence of a random array of acceptor molecules can be predicted theoretically. Although the original treatment of Inokuti and Hirayama²⁰ dealt

(18) Perrin, F. C. *R. Hebd. Seances Acad. Sci.* **1924**, 178, 1978-1980.

(19) Anderson, C. P.; Salmon, D. J.; Meyer, T. J.; Young, R. C. *J. Am. Chem. Soc.* **1977**, 99, 1980-1982.

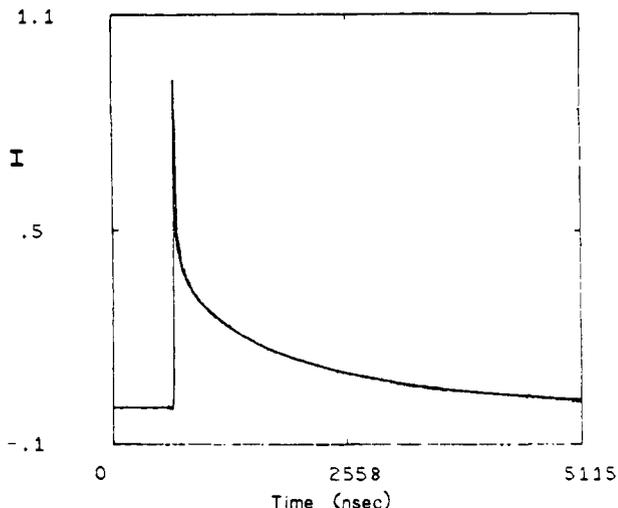


Figure 4. Luminescence decay of $\text{Ru}(\text{ester})_3\text{Cl}_2^*$ in the presence of 0.0728 M TMPD (TMPD = 1.36) in Lexan. Superimposed on the experimental decay curve is a theoretical fit to eq 8. The fit was obtained by allowing both γ and the initial intensity to float. The curve shown corresponds to $\gamma = 18$ ($\alpha = 0.5 \text{ \AA}^{-1}$).

with energy transfer, the result is entirely analogous to electron-transfer processes.^{3b-d} Several assumptions are implicit in the following treatment: (1) Translational motion is slow. (2) Hopping processes are inefficient. (Donor-donor transfer is negligible). (3) Effects of molecular orientation are negligible.

In the absence of quencher, the luminescence decay of the donor is assumed to be exponential. Thus, the probability of a donor being excited at time t is

$$P(t) = \exp(-t/\tau_0) \quad (7)$$

where τ_0 is the excited-state lifetime. When quencher is present, the decay is much faster due to the additional decay mode of electron transfer. At $t = 0$, the emission intensity is the same in the presence and absence of quencher, since the probability of instantaneous emission is unchanged. At short times, the luminescence decay is more rapid due to the quenching of donors by nearby acceptors. However, at longer times, the number of donors having nearby acceptors is depleted, and the decay approaches that of an unperturbed system (no quencher). The net result is that the time evolution of luminescence decay is grossly nonexponential. In the case of a totally random acceptor distribution, it is given by²⁰

$$\phi(t) = \exp[-t/\tau_0 - \gamma^{-3}c/c_0g(e^{\gamma t}/\tau_0)] \quad (8)$$

where $\gamma = 2R_c\alpha$, c = quencher concentration, and c_0 is the critical quencher concentration (the concentration at which the average donor-acceptor distance = R_c^{obsd}). The function $g(z)$ can be evaluated numerically.²⁰

$$g(z) = (\ln z)^3 + 1.73(\ln z)^2 + 5.93(\ln z) + 5.44$$

The experimental decay curve of one of the $\text{Ru}(\text{LL})_3^{2+*}/\text{D}$ reactions, $\text{Ru}(\text{ester})_3^{2+*}$ in the presence of TMPD, was fitted to eq 8, resulting in $\gamma = 19 \pm 3$ ²¹ (Figure 4). Thus, $\alpha = 0.5 \pm 0.01 \text{ \AA}^{-1}$ which corresponds to a barrier height of 1 eV. This is much smaller than the roughly 5 eV barrier to electron transfer expected from the measured TMPD ionization potentials.²²

In order to fully determine how α depends on donor ionization potentials, equally detailed experiments of all the $\text{Ru}(\text{LL})_3^{2+*}/\text{D}$ reactions should be performed. Therefore, we studied the luminescence quenching of $\text{Ru}(\text{me}_2\text{phen})_3\text{Cl}_2$ by TMPD (Figure 5). This reaction is much less exothermic: $\Delta\Delta G \sim 0.75 \text{ V}$. A fit of the luminescence decay gives $\alpha = 0.64 \pm 0.1 \text{ \AA}^{-1}$. It appears, then, that the increased (hole) binding energy in the Ru -

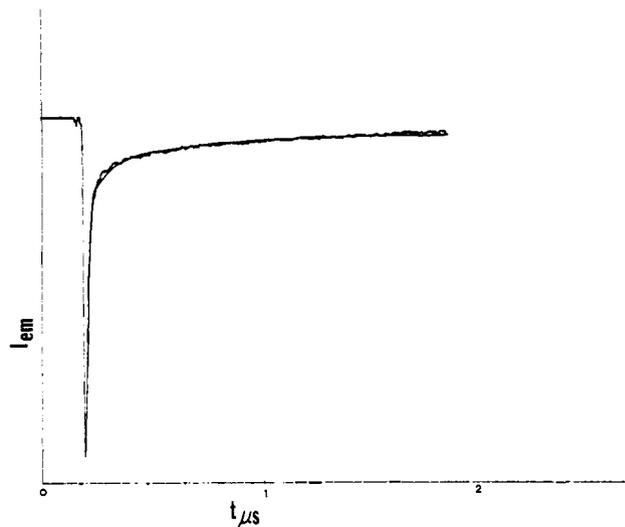


Figure 5. Luminescence decay of $\text{Ru}(\text{me}_2\text{phen})_3\text{Cl}_2/\text{TMPD}$ ([TMPD] = 1.75(Co)) in Lexan. The data are fit to $\gamma = 15$ ($\alpha = 0.6 \text{ \AA}^{-1}$).

(me_2phen) $_3\text{Cl}_2$ compound results in an increase in α . However, this result must be viewed with caution for three reasons. First, and most obviously, the difference between $\alpha = 0.50 \pm 0.07$ and $\alpha = 0.64 \pm 0.1 \text{ \AA}^{-1}$ is within experimental error.

Second, the line shape at low exothermicity can be influenced not only by the dependence of rate on distance but also by the time dependence of relaxation of the medium. This effect is negligible when $\Delta G \approx \lambda$, but can become significant when $\Delta G \ll \lambda$. In principle, then, α values should only be compared at equivalent exothermicities, preferably at $\Delta G \approx \lambda$. Such comparisons are not possible with the present systems.

Finally, in the me_2phen complex, a small nonexponential decay component was observed in the absence of TMPD. Such nonexponentiality introduces another adjustable parameter into the line shape analysis, which significantly reduces the reliability of this analysis.

Time-resolved experiments with $\text{Ru}(\text{ester})_3^{2+*}/\text{D}$ pairs, where D are organic reductants besides TMPD, are all expected to have electronic terms H_{ab} very similar to that of the $\text{Ru}(\text{ester})_3^{2+*}/\text{TMPD}$ reaction.

Conventional barrier transfer (eq 1-3) suggest that α depends strongly on donor ionization potential V : $\alpha \approx V^{1/2}$. For the reaction $\text{Ru}(\text{ester})_3^{2+*}/\text{TMPD}$, TMPD is the ground-state donor and V is measured to be $\sim 5.8 \text{ eV}$.²² According to the barrier tunneling model, α for this reaction should be about 1.2, which is in contrast with the experimental result $\alpha = 0.5$ mentioned above. However, Beitz, and Miller²³ have pointed out that an alternative charge-transfer mechanism is possible, which involves positive (hole) charge transfer (analogous to valence band conduction in semiconductors). In this mechanism the electronic interaction term H_{ab} is given by $H_{ab} = \beta_+(\beta_+/B_+)^n$ where n is the number of steps of size d between the donor and acceptor: $d \cdot n = R_{d-A}$. For a random solvent, d would be estimated by the size of the solvent molecules. B_+ is the hole binding energy and β_+ the coupling strength for each of the individual n interactions. Using this model $\alpha = 1/d \ln(B_+/\beta_+)$. For $\alpha = 0.5$, $\beta = 80 \text{ cm}^{-1}$ and $d = 9 \text{ \AA}$ (i.e.: 1 monomer unit) $B_+ \approx 1 \text{ V} = \text{IP}_{\text{lexan}} - \text{IP}_{\text{Ru}^{2+}}$. An important difference between the superexchange model and tunnelling across a simple barrier involves the dependence of the electronic coupling (distance) term α on donor ionization potential V . For example, in a barrier tunneling model when $B_+ = 1 \text{ V}$ $\alpha = 0.5$, and when $B_+ = 1.8 \text{ V}$ $\alpha = 0.67$. By comparison in the superexchange model, when $B_+ = 1 \text{ V}$ $\alpha = 0.5$, but when $B_+ = 1.8 \text{ V}$ $\alpha = 0.56$. (If B_+ is increased (and d correspondingly

(20) Inokuti, M.; Hirayama, F. *J. Chem. Phys.* **1965**, *43*, 1978-1989.

(21) Guarr, T.; Strauch, S.; McLendon, G., unpublished results.

(22) Bernas, A.; Gautheri, M.; Grand, D.; Parlant, G. *Chem. Phys. Lett.* **1972**, *17*, 439-443.

(23) Miller, J. R.; Beitz, J. V. *J. Chem. Phys.* **1981**, *74*, 6746-6756.

(24) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1-64.

decreased) then a 0.8 V change in binding energy will change α by even less.)

Within the experimental uncertainties, both the superexchange and barrier tunneling descriptions are consistent with the time-resolved data. For a square barrier, $\alpha \propto V^{1/2}$ while for superexchange $\alpha \propto \ln V$.

In order to distinguish the superexchange and barrier tunnelling models, the dependence of electron (hole) transfer rate at a given distance on donor ionization potential was examined for a range of compounds. We have carried out such a study by varying the potential, ΔE , of either the (hole) donor (Ru(LL)₃^{2+*}/TMPD series) or acceptor (Ru(ester)₃^{2+*}/D series) (Table I). When the donor energy is changed, this change affects both the Franck-Condon factor *and* the electronic coupling term H_{ab} . When only the acceptor energy is varied, (the Ru(ester)₃^{2+*}/D series), the Franck-Condon factors change, but H_{ab} and thus α remain essentially constant.

Figure 3 graphically depicts the rates of both of the above series of reactions and shows that a very similar dependence of rate (R_c) on ΔE is observed regardless of whether the donor energy or acceptor energy is varied. This result demonstrates that within experimental error, changing ΔE solely affects the Franck-Condon term and not the electronic term H_{ab} in eq 1. This result is consistent with a superexchange model, but *not* with a barrier tunnelling model.

If a barrier tunnelling model were assumed, with $\alpha \propto V^{1/2}$, then the relative critical distances for the two approximately equienergetic reactions (1) Ru(phen)₃^{2+*}/TMPD and (2) Ru(ester)₃^{2+*}/DMT can be calculated as follows. For reaction 2, we take $2\alpha = 1.0 \text{ \AA}^{-1}$, as experimentally measured (vide supra). Thus the binding energy is $\sim 1 \text{ eV}$. For reaction 1, the binding energy is $\sim 1.6 \text{ eV}$, and thus 2α is calculated to be $\sim 1.3 \text{ \AA}^{-1}$. At the critical distance for each reaction, the rate constants for each reaction are essentially equal;

$$k(1) = \text{FC} \exp(-1.3R_1) = k(2) = \text{FC} \exp(-1.0R_2) \quad (9)$$

If $R_2 = 13.1 \text{ \AA}$, as observed, R_1 must be $\sim 10.5 \text{ \AA}$ in eq 9 to be consistent with the Gamow tunnelling model. Instead, $R_1 = 13.7 \text{ \AA}$! Thus, the data in Figure 3 are more consistent with a superexchange description of hole transfer.

A second piece of information obtained from Figure 3 is the total reorganization energy. From the maximum in the ΔE vs. R_c curve, $E_r \approx 1.0 \pm 0.2 \text{ V}$ for reduction of Ru(LL)₃^{2+*} by substituted aromatic anilines. A value of $\lambda = 1.1 \text{ V}$ effectively reproduces the observed differences in R_c for different ΔG values. The reorganization energy includes an inner-sphere component, E_c , which reflects bond reorganizations of the reactants, and a medium reorganization energy, E_s , which reflects medium repolarization around the charge centers. E_s can be readily calculated from classical theory:^{1c}

$$E_s = (\Delta e)^2 (1/D_{op} - 1/D_s) (1/2R_D + 1/2R_A - 1/R) \quad (10)$$

D_{op} = optical dielectric = (refractive index)², D_s = static dielectric constant of medium (~ 2.5 for Lexan), Δe = number of electrons transferred, R_D = radius of donor, R_A = radius of acceptor, and R = donor-acceptor distance at which electron transfer occurs.

For $R \approx 19 \text{ \AA}$, $E_s \approx 0.2 \text{ V}$. Slightly smaller E_s values will apply at smaller R values.

Consideration of the internal reorganization energy, E_c , is more complex. E_c reflects the energy required to reorganize the reactant bond lengths and angles to produce products. E_c thus depends on the changes in equilibrium bond lengths (or angles) between reactants and products, and on the frequencies of the bonds which change:

$$E_c = \sum f_i \Delta r_i^2 \quad (11)$$

where f_i is the force constant for the i th bond and Δr_i is the bond displacement. For the TMPD/TMPD⁺ couple, for example, the necessary values of f_i and Δr_i are available from literature studies.²⁵

(25) Ikemoto, I.; Katagiri, G.; Nishimura, S.; Yakushi, K.; Kuroda, H. *Acta Crystallogr., Sect. B: Struct. Sci.* **1979**, *35*, 2264-2265.

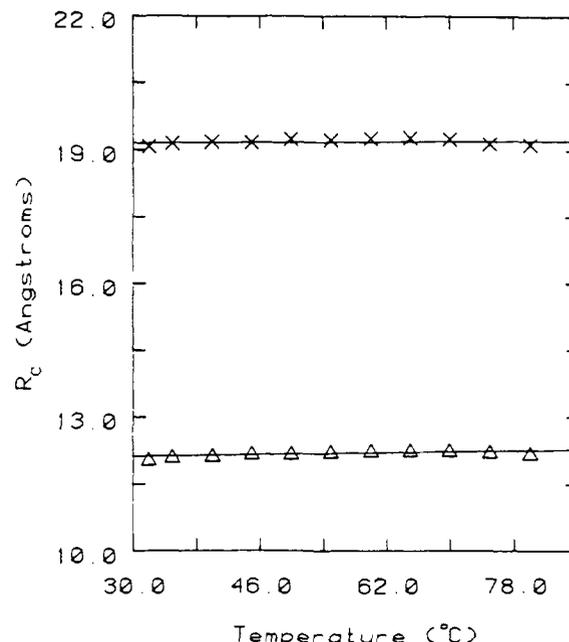


Figure 6. Plot of R_c^{cor} vs. temperature from 300K-350K for the reactions of Ru(ester)₃^{2+*} (X) and Ru(Me₂phen)₃^{2+*} (Δ) with TMPD in Lexan.

These values together with eq 11 lead to $E_c = 0.4 \pm 0.1 \text{ V}$ for TMPD. Other TMPD homologues used in this paper are assumed to have similar structural and electronic properties, and thus similar E_c values. For the (RuL₃)^{2+*/+} couple such data are not generally available. However, it is expected that E_c will be quite small for this couple, for the following reason. The redox active charge-transfer state of (RuL₃)^{2+*} homologues has been shown to involve an electron localized on the bipyridine ligand, i.e.: RuL₃^{2+*} \approx L₂Ru^{III}L⁻.^{26,27} The monocation species has been similarly characterized as containing a bipyridine anion radical.²⁶ Time resolved resonance raman studies (TR³)²⁷ have underscored the strong structural similarity between the charge-transfer state and the singly reduced complex. Thus, any reorganization which occurs in the reaction (RuL₃)^{2+*} + e⁻ → (RuL₃)⁺ effectively involves primarily bond length changes between (Ru^{III}L₂L⁻)* and (Ru^{II}L₂L⁻). These are known to be negligible.²⁸ Given the lack of *definitive* structural data, prudence dictates an estimate of $0.1 \pm 0.1 \text{ V}$. We thus obtain an estimate $E_c = 0.5 \pm 0.2 \text{ V}$. However, this *internal* reorganization energy solely involves high-frequency modes, $\hbar\omega \geq 1200 \text{ cm}^{-1} \geq 6kT$. Thus, these modes are essentially "frozen" in the ground vibrational state near ambient temperatures, and reorganization involving these modes occurs primarily via nuclear tunneling.

Temperature Dependence. A stringent test of the validity of the reorganization parameters is provided by studies of the temperature dependences of these reactions. From theoretical simulations, only reactions with $\Delta E < 0.1 \text{ V}$ show any appreciable temperature dependence, mostly below $\sim 300 \text{ K}$. We have studied the reactions of Ru(ester)₃^{2+*} and Ru(Me₂phen)₃^{2+*} with TMPD ($\Delta E = 0.88$ and 0.13 V , respectively) at 77 and 298-350 K, and the Ru(5-Clphen)₃^{2+*}/TMPD system ($\Delta E = 0.49 \text{ V}$) at 77 and 298 K in order to compare experimental results with theoretical predictions.

Figure 6 shows the results of the Ru(ester)₃^{2+*}/TMPD and Ru(Me₂phen)₃^{2+*}/TMPD experiments for the temperature range 300-350 K. As predicted, neither reactions show a significant

(26) Tokel-Takvoryan, N. E.; Hemingway, R. E.; Bard, A. J. *J. Am. Chem. Soc.* **1973**, *95*, 6582-6589.

(27) Forster, M.; Hester, R. E. *Chem. Phys. Lett.* **1981**, *81*, 42-47.

(28) Caspar, J. V.; Westmoreland, D. T.; Allen, G. H.; Bradley, P. G.; Meyer, T. J.; Woodruff, W. H. *J. Am. Chem. Soc.* **1984**, *106*, 3492-3498.

(29) Frese, K. W., Jr. *J. Phys. Chem.* **1981**, *85*, 3911-3916.

(30) Smoluchowski, M. von. *Z. Phys. Chem., Stoechiol. Verwandtschaftsl.* **1917**, *92*, 129.

dependence of rate on temperature $E_{act} < 2$ kcal/M. These results provide an interesting comparison with studies of hopping charge transport in molecularly doped Lexan.³¹ In such studies where $\Delta G \geq 0.01$ V due to the electric field gradient, $E_{act} \geq 10$ kcal/M.

However, when all three of the reactions mentioned above were compared at room temperature and 77 K, a significant temperature dependence is observed, which is larger than expected from simple Marcus theory. We believe these lower reaction rates reflect the slow dielectric response of the β relaxation at low temperature, which may lead to a change in the effective frequency factor for reaction.^{4,31}

Summary. We have observed long distance nonadiabatic electron (hole) transfer for the reactions $(Ru(LL)_3)^{2+*}$ + organic reductants in rigid polycarbonate medium. The transfer distances appear to be larger than in the $(Ru(LL)_3)^{2+*}/MV^{+2}$ oxidative quenching reactions observed in rigid glycerol.^{3a} The reactions in polycarbonate appear to be more accurately described by the

superexchange mechanism, with the primary reaction path being hole transfer from the $(Ru(LL)_3)^{2+*}$ to the organic reductant mediated through positive solvent states. In the superexchange mechanism, the electronic damping factor α is proportional to $\ln V$, where V is the hole binding energy of the Ru complexes. This mechanism gives more satisfactory results than conventional electron tunnelling theories, which predict $\alpha \propto V^{1/2}$, where V is the ionization energy of the organic reductant.

The temperature of these reactions in Lexan show predicted behavior from ~ 300 to 350 K. However, at low temperatures, these reactions tend to show "solvent controlled" rates which are a function of the dielectric response of the medium. This behavior has been observed in other systems.⁴

Acknowledgment. This work was supported by the National Science Foundation. Further support was provided by the Sherman Clarke fellowships of the University of Rochester to Tom Guarr and Mark McGuire. We are grateful to John Miller for detailed and insightful discussions of this work, particularly with regard to questions of ΔE estimation.

(31) Stolka, M.; Yanus, J.; Pai, D. *J. Phys. Chem.* 1984, 88, 4707.

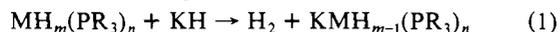
A Lipophilic Salt of a Transition-Metal Polyhydride: $KOsH_3(PMe_2Ph)_3$

John C. Huffman, Mark A. Green, Susan L. Kaiser, and Kenneth G. Caulton*

Contribution from the Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405. Received February 12, 1985

Abstract: The polyhydride OsH_4P_3 ($P = PMe_2Ph$) is deprotonated by KH in THF to yield $K[fac-OsH_3P_3]$, characterized by 1H and ^{31}P NMR spectroscopy. This reaction also proceeds in aromatic solvents, and the ether-free product is soluble in benzene and toluene. Spectral properties in toluene are similar to those in THF but reveal subtle differences. The crystal structure of $KOsH_3(PMe_2Ph)_3$, crystallized from toluene, reveals the reason for the lipophilic character of this material. It consists of centrosymmetric $K_2Os_2H_6(PMe_2Ph)_6$ dimers composed of $(PhMe_2P)_3Os(\mu-H)_3K$ monomers (an intimate ion pair) bound into dimers by one additional hydride bridge from each K to one hydride hydrogen in the second monomer unit. Equally important to the dimerization is the enfolding of each K^+ by two phenyl rings of the second monomer unit with the result that the periphery of the molecule is entirely hydrocarbon in character. The hard acid/soft base character of the K^+ /phenyl interaction is particularly surprising. Crystal data for $KOsH_3(PMe_2Ph)_3$ (at -160 °C) are the following: $a = 9.990$ (2) Å, $b = 22.867$ (8) Å, $c = 12.381$ (3) Å, $\beta = 111.44$ (1)° with $z = 4$ in space group $P2_1/n$.

In the course of studying the synthesis of *anionic* transition-metal polyhydride complexes by the deprotonation of neutral polyhydrides¹ with KH (eq 1), we have been accustomed to em-



ploying tetrahydrofuran as solvent, both to promote this polar reaction and also because we expected the polyhydride anion salt to be soluble in this solvent. While these expectations are born out for $OsH_4(PMe_2Ph)_3$ as the conjugate acid in eq 1, we were most surprised to find that this proton transfer also proceeds in toluene solvent *and* that the product has good solubility in this medium. We describe here the full characterization of $KOsH_3(PMe_2Ph)_3$ and the explanation of how such a material can achieve solubility in aromatic hydrocarbons. At the same time, this work provides a rare structural view of the manner in which contact ion pairs aggregate to larger units.

Experimental Section

General. All manipulations were carried out in an atmosphere of prepurified N_2 (BASF R-311 purification bed) with solvents dried over benzophenone ketyl (THF) or liquid NaK alloy (arenes). In order to avoid protonation of the very basic anion, glassware should be flamed

under vacuum. Reliable spectroscopic measurements are best done in NMR tubes which have been prerinsed with a sacrificial charge of $KOsH_3(PMe_2Ph)_3$ solution. Alternatively, since the $OsH_3P_3^-/OsH_4P_3$ equilibrium is reversible, this conjugate pair in the presence of excess KH may be used to scavenge surface bound protons. ^{31}P chemical shifts *downfield* of the 85% H_3PO_4 reference signal are given *positive* values.

$K[fac-OsH_3(PMe_2Ph)_3]$. To a THF solution of $OsH_4(PMe_2Ph)_3$ in an NMR tube was added a threefold excess KH powder (prepared from a 35% dispersion of KH in mineral oil by the procedure described in the literature),² and the solution was heated in a 70 °C oil bath for 12 h. ^{31}P and 1H (when reaction was done in THF- d_8) NMR spectra showed quantitative conversion to yellow $K[fac-OsH_3(PMe_2Ph)_3]$. The excess KH was easily removed by filtration; however, in the absence of KH, the product slowly transforms to $OsH_4(PMe_2Ph)_3$ on standing even in oven-dried glassware. Addition of H_2O to a THF solution of $K[OsH_3(PMe_2Ph)_3]$ gave immediate quantitative (^{31}P NMR) conversion to $OsH_4(PMe_2Ph)_3$. The product also reacts rapidly with acetonitrile- d_3 to generate $OsH_xD_{4-x}(PMe_2Ph)_3$. NMR data for $K[fac-OsH_3(PMe_2Ph)_3]$ follow: in tetrahydrofuran- d_8 , $^{31}P\{^1H\}$ NMR (30 °C) δ -30.1 (s), 1H NMR (220 MHz, 16 °C) δ 7.89 (t, $J = 7$ Hz, 6 H, *o*- C_6H_5), 7.20 (m, 9 H, *m*- and *p*- C_6H_5), 1.54 ($J = 6$ Hz, 18 H, *P*- CH_3), -11.60 (m, 3 H, *Os*-H); in toluene- d_8 H 7.69 (br), 7.2 (br), 1.79 (br), -11.88 (m), ^{31}P -32.5.

(1) Bruno, J. W.; Huffman, J. C.; Green, M. A.; Caulton, K. G. *J. Am. Chem. Soc.* 1984, 106, 8310.

(2) Inkrott, K.; Goetze, R.; Shore, S. G. *J. Organometal. Chem.* 1978, 154, 337.