Communications to the Editor

Collisionless Photoinduced Electron Transfer from Ruthenium Tris(bipyridine)$^{2+*}$ Homologues to Methyl Viologen (MV^{2+}) in Rigid Glycerol Solution

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Considerable and continuing progress has been made in the theoretical[1-6] and experimental[2,7-9] treatment of electron-transfer reactions. One key question that remains is "How does the electron-transfer rate depend on distance?"[7c] or equivalently "Over what distance can electron transfer occur within a given time period?" This question can only be meaningfully answered when several key experimental variables are defined, including the temperature, reaction driving force (ΔE), and molecular reorganization energy (E_r). Current theories of nonadiabatic electron transfer suggest that electron-transfer rates decrease exponentially with distance. A short synopsis specific to the present case is given below.

In the high-temperature, strong coupling limit, which applies to the present experiments,[5,6] the electron transfer rate, W, is

$$W = A \exp[-(\Delta E - E_r)^2/4E_r kT] \qquad (1)$$

The exponential term describes the activation energy in terms of the driving force for reaction, ΔE, and the reorganization energy, E_r, due to redox-induced changes in the structures of the reactants or of the solvent. This equation is based on several experimental assumptions. First of all, the high-temperature limit implies that $kT \gg \hbar\omega_s$. This in turn requires that the intramolecular contribution to the reorganization energy (E_r) be small, i.e., bond-length changes are small on oxidation–reduction. In this case the reorganization energy is dominated by low-frequency solvent polarization modes ($\hbar\omega_s < 10$ cm^{-1} for H_2O). Note that the high-temperature thermally activated rate expression is equivalent to the classical (Marcus) expression.[1] The second assumption is that strong electronic–vibrational energy coupling occurs: $E_r = S\hbar\omega$, with $S \gg 1$.[5,6] This strong coupling seems ubiquitous in polar media like water or glycerol.[5,6]

Table I. Quenching Radii, Emission Lifetimes, and Redox Potentials of the $[Ru^{II}L_3]^{2+}$ Homologues

complex	ΔE,[a] V	τ_0,[b] μs	R_q,[c] Å	R_q,[d] Å
I, L = 5-chlorophenanthroline	0.35	3.0	10.6	12.2
II, L = bipyridine	0.42	1.2	10.9	13.1
III, L = 4,4′-dimethylbipyridine	0.6	0.90	12.0	14.1
IV, L = 3,4,7,8-tetramethylphenanthroline	0.7	3.2	15.0	15.5
V, L = (terpy)(bpy)NH_3	1.0	2.0	13.0	14.2

[a] Overall potential for the reaction $[RuL_3]^{2+*} + MV^{2+} \rightarrow MV^{+\cdot} + [RuL_3]^{3+}$ (see ref 11). [b] Lifetime in dry glycerol solution, ~0 °C. These lifetimes, determined by laser flash techniques, differ significantly from those in aqueous solution at ambient temperatures. [c] R_q = Perrin "critical distance" between molecular centers (see text). At $R < R_q$, all excited states are deactivated by electron transfer. The edge–edge distance between the donor and acceptor is estimated as $R_q - 10 \pm 1$ Å from the known structures of the ruthenium homologues and methyl viologen. [d] R_q normalized to a 1 μs lifetime for all complexes. Assume $R_q = R_0 + a \ln \nu_0$; $a = 0.7$.[7] A correction for finite molecular volume is also included: $(R_q^{\text{obsd}})^3 + R_0^3 = (R_q^{\text{corr}})^3$; $R_0 = 10 \pm 1$ Å

The prefactor, A, gives the dependence of electron-transfer rate on distance between redox partners:

$$A = 2\pi|V|^2/h^2\omega \qquad V = V_0 \exp(-\alpha R) \qquad (2)$$
$$V_0 \cong 1.0 \times 10^5 \text{ cm}^{-1}$$

Here we report a simple approach to the problem of electron-transfer reaction distances based on studies of photoinduced electron transfer in a rigid solution. Several previous studies have examined electron transfer in rigid solution induced by light[8] or by pulse radiolysis.[7,18] In most previous studies, however, either ΔE was poorly defined or the dependence of rate on ΔE was complicated by the use of nonhomologous donor/acceptor pairs.[10]

The electron donors in this study are chosen from the well-studied series of ruthenium polypyridine homologues. The photophysical and electron-transfer properties of these complexes have been studied in detail.[11] Thus, the energetics of excited-state electron transfer are fully characterized (Table I). In particular, the use of this homologous series allows the reaction driving force (ΔE) to be accurately determined and systematically varied, while all other parameters are held as constant as possible. The electron acceptor was *N,N′*-dimethyl-4,4′-bipyridine (methyl viologen, MV^{2+}).

The redox chemistry and electronic structure of MV^{2+} have also been fully characterized.[12] In particular, the lowest MV^{2+} excited state is 20 000 cm^{-1}.[13] Therefore, RuL_3^{2+*} deactivation can occur only by electron transfer and not by energy transfer.

Experimental Methods. $Ru(bpy)_3Cl_2$ (GF Smith Co.) was used as received. The other RuL_3^{2+} homologues (L = 5-chlorophenanthroline, 4,4′-dimethylbipyridine, 3,4,7,8-tetramethylphenanthroline) were prepared by procedures similar to those used by Sutin et al.[14] Ru(terpy)(bpy)NH_3 was prepared by a procedure

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(10) After this work was completed, we learned of independent work by Miller and co-workers in which the quenching of organic dyes with known ΔE has been studied in rigid (decalindiol) solution. Miller's conclusions are in qualitative agreement with those reported above.

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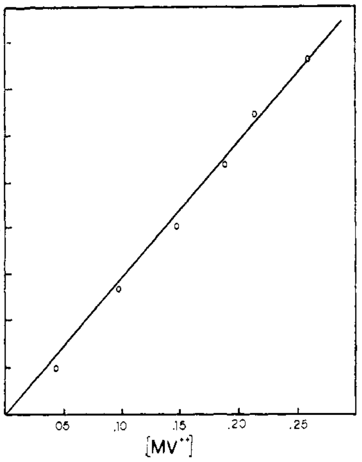

Figure 1. Plot of the emission intensity quenching ln (I_0/I) of Ru$(bpy)_3^{2+*}$ vs. molar concentration of MV^{2+}. The data are taken at −12 °C, whence the translational motion during the Ru* lifetime is ca. 0.7 Å. Similar plots are obtained at all temperatures at or below 3 °C, for all the complexes examined.

developed by Meyer.[15] Methyl viologen (Aldrich) was recrystallized twice from 95% EtOH and washed with cold 99% EtOH. Spectrograde glycerol (Fisher) was distilled under low pressure (~25 torr).

RuL_3^{2+} and MV^{2+} were codissolved in dry distilled glycerol and cooled to $248\ K \le T\ 276\ K$. The ruthenium concentration was held constant at ca. 10^{-5} M, while the MV^{2+} concentration was varied from 0.05 to 0.5 M. The average center–center distance (Å) between the excited-state $[RuL_3]^{2+*}$ electron donor and the methyl viologen electron acceptor is thus

$$\bar{R} = (3 \times 10^{27}/4\pi[MV^{2+}]N)^{1/3} \tag{3}$$

where $[MV^{2+}]$ is the molar concentration of methyl viologen and N is Avogadro's number. Under our conditions the glycerol viscosity η is 2.3×10^5 cP > η > 8.3×10^3 cP. The maximum accessible translational distance $R_t = (2D_0t)^{1/2}$. Thus, since τ_0 for the RuL_3^{2+*} reactive excited state ranges from 9.0×10^{-7} to 3.2×10^{-6} s, and by estimation of $D_0 < 10^{-10}$ cm²/s, R_t ranges from 0.3 Å < R_t < 1.3 Å for Ru$(4,4'\text{-}Me_2bpy)_3^{2+}$ to 0.5 Å < R_t < 2.0 Å for Ru$(3,4,7,8\text{-}Me_4phen)_3^{2+}$. Thus the average center-to-center distance as calculated by eq 3 is relatively fixed under our experimental conditions.

Electron transfer was monitored by using a Perkin-Elmer MPF-44A spectrofluorimeter and measuring the methyl viologen dependent quenching of the excited-state ruthenium emission intensity (I). The quenching efficiency (I_0/I) provides a direct probe of electron-transfer rates when the rate of electron transfer competes with the rate of radiative deactivation of the excited state.

Results and Discussion. The data may be interpreted by the "capture volume" model, first proposed by Perrin.[16] A rigorous quantum description of the capture-volume model has been developed by Inokuti and Hirayama[17] and applied by Miller and others to electron transfer in rigid matrices.[10,18] This model is briefly reviewed below.

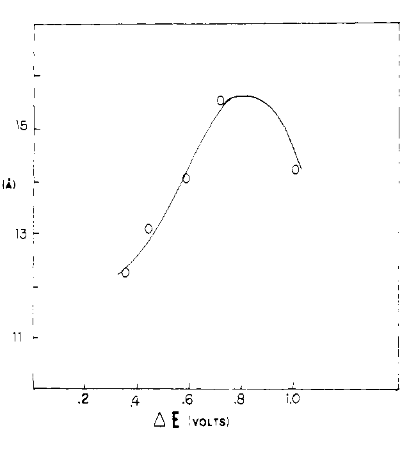

Figure 2. Plot of critical distance, R_q, (corrected for molecular volume and normalized to 1 μs τ_0) vs. driving force for the reactions $RuL_3^{2+*} + MV^{2+} \rightarrow MV^{+\cdot} + RuL_3^{3+}$: (1) L = 5-chlorophenanthroline; (2) L = bipyridine; (3) L = 4,4′-dimethylbipyridine; (4) L = 3,4,7,8-tetramethylphenanthroline; (5) L = (terpyridyl)(bipyridyl)ammine.

Let R_q be the donor–acceptor distance (in centimeters) such that the rate of electron transfer (W) from the excited-state electron donor to the acceptor is $W = 1/\tau_0$, where τ_0 is the emission lifetime of RuL_3^{2+*} in the absence of quencher. The electron-transfer rate depends steeply on distance; $W = C\exp(-R/a)$, where C and a are constants and $a = 1/\alpha$. The parameter a has the same units (Å) as R. The best estimates available from pulse radiolysis studies suggest $a \simeq 0.75$ Å.[7,18] Given this steep distance dependence, when $R_q \gg a$, emission from any donor with an acceptor at a distance $R < R_q$ will be totally quenched, while all donors with acceptors at a distance $R > R_q$ will emit with lifetime $\tau = \tau_0$ (and emission intensity $I = I_0$). Thus, although R_q is an average, averaging occurs over a narrow range when $R_q \gg a$. The observed emission intensity is then $I_0/I = \exp(4\pi/3[A]R_q^3) = \exp(R_q/\bar{R})^3$, where [A] is the acceptor concentration in molecules/cm³. As Figure 1 shows, this model quite accurately describes the data.[16] It is clear from the R_q values listed in Table I that electron transfer on the microsecond time scale occurs over only short distances. For example, for the reaction $Ru(bpy)_3^{2+*} + MV^{2+} \rightarrow MV^{+\cdot} + Ru(bpy)_3^{3+}$, R_q = 13.1 Å, corresponding to a separation of ~3 Å between the edges of the reactants.

However, as the reaction driving force, ΔE, increases, the effective quenching distance, R_q, and associated electron-transfer rate rise rapidly (Table I). (Note that, for a = 0.75 Å, a change in R_q of 1.7 Å corresponds to a 10-fold change in rate.) The effect of changing ΔE is summarized in Figure 2. On going from ΔE = 0.35 V to ΔE = 0.7 V, R_q increases by ca. 3 Å. For a = 0.75 Å, this corresponds to an effective 50-fold increase in rate, in good agreement with the classically calculated ratio.[20]

The maximum rate and corresponding maximum distance should be obtained when $\Delta E = E_r$. An estimate of the reorganization energy can be obtained from data in fluid solution, as tabulated by Frese.[21] These data suggest $E_r \approx 0.7 \pm 0.1$ V. However, these estimates must be corrected for the fact that the solvent reorganization energy will increase as the donor–acceptor separation increases. With the formula of Marcus[22] at $R_q \approx 15$ Å, $E_r \approx 0.8 \pm 0.1$ V. A maximum rate is thus expected for the $Ru(Me_4phen)_3^{2+}/MV^{2+}$ couple. Preliminary data suggest an apparent *decrease* in R_q (or W) at ΔE = 1.0 V, with Ru$(trpy)(bpy)NH_3^{2+}$ as the electron donor. This may simply reflect a peculiarity of the $Ru(trpy)(bpy)NH_3^{2+}$ system. However, it may also signal the onset of the Marcus "inverted" region. Previous attempts to probe the inverted region via excited-state reactions did not demonstrate inverted kinetic behavior.[23]

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(19) When neutral ruthenium complexes were used, e.g. $Ru(bpy)_2(CN)_2$, donor–acceptor adducts were formed, characterized by strong emission at λ 550 nm. The properties of these adducts will be described in detail elsewhere. Some limited adduct formation was also observed at $[MV^{2+}] > 0.1$ m for the most easily oxidized Ru(II) complex. Only data were analyzed for which no donor–acceptor emission was observed (i.e., the concentration of donor–acceptor complexes was <1%).

(20) In the simplest treatment[1] (ignoring the quadratic term in eq 1), the rate should increase by $10\Delta[\Delta E/0.059]^{1/2}$. For $\Delta(\Delta E) = 0.7 - 0.35 = 0.35$, a rate increase of ca. 10^3 is expected. Including the quadratic term decreases this ratio to ca. 20.

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However, Marcus and Siders have pointed out[22] that the rate decrease in the inverted region will be largely smoothed out by diffusion. Thus, inverted behavior would be best observed in a diffusion-free medium, as in the present case. Clearly, further studies at $\Delta E > 0.8$ V are necessary and are in progress.

In summary, the data show that electron transfer between ruthenium polypyridyl homologues and MV^{2+} occurs over rather limited distances on the microsecond time scale. The present report is inconsistent with suggestions of 30-Å electron-transfer distances in vesicles.[9a] However, the accessible distance can be strongly modulated by ΔE, in quantitative agreement with modern theories of electron transfer. Our results are largely consistent with analogous studies by Miller et al.,[10] who observed reaction distances of up to 15 Å (center-center) by monitoring luminescence quenching of organic dyes. Interestingly, in their system, Miller et al. observe somewhat faster rates at equivalent distances and ΔE values. Finally, we note the intriguing possibility in such experiments of observing reactions in the inverted region. Present experiments are focused on this possibility.

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Registry No. I, 47860-47-9; II, 15158-62-0; III, 32881-03-1; IV, 64894-64-0; V, 58452-44-1; MV^{2+}, 4685-14-7.

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Thermal Fragmentation of Silacyclobutane. Formation of Silylene, Methylsilylene, and Silene

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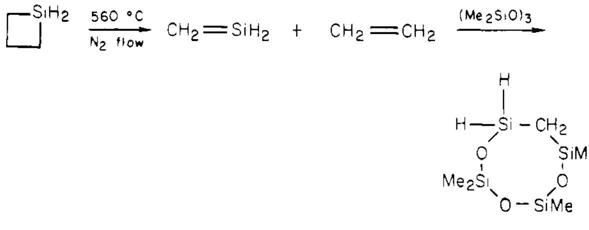
Although the thermal decomposition of the unsubstituted silacyclobutane has been studied by several groups,[1-5] only in the original work of Sommer and co-workers was a silicon-containing product identified. Evidence for the parent silene, anticipated from the 2 + 2 fragmentation of silacyclobutane, was based on the isolation of a product from addition of a silicon-oxygen σ bond across the silicon-carbon π bond (eq 1). We report here that thermal decomposition leads not only to silene as previously suggested but predominantly to methylsilylene (SiHCH$_3$) and also the parent silylene (SiH$_2$; eq 2).



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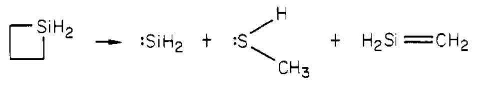
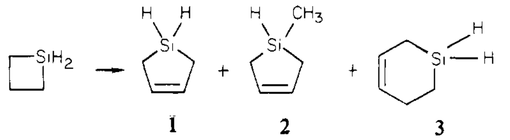


(2)

Table I. Temperature Dependence of Product Formation



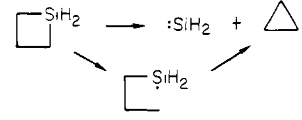
1 2 3

T, °C	decomp,^{a} %	yield,^{a} % 1	2	3	product ratios 1:(2 + 3)	2:3
556	16	1.9	5.9	5.1	0.17	1.2
600	34	4.8	14.1	7.6	0.22	1.9
650	67	9.9	29.9	13.1	0.23	2.1
697	97	13.7	49.1	9.7	0.23	5.1

^{a} Percent decomposition and percent yield were measured relative to hexane as an inert internal standard and based on the amount of silacyclobutane decomposed.

Pyrolyses were carried out with a 10-fold excess of 1,3-butadiene in a high-vacuum flow system[6] to optimize efficiency of trapping the primary fragments from silacyclobutane. Over the temperature range 556-697 °C, three silicon-containing products were formed from reactions with butadiene as shown in Table I. Both silacyclopent-3-ene[7] (**1**) and 1-methyl-1-silacyclopent-3-ene[7] (**2**) are products previously observed from reactions of the respective silylene and methylsilylene with butadiene. The third product, silacyclohex-3-ene[8] (**3**), is the 2 + 4 adduct expected from silene and butadiene.

At 556 °C the elimination of silylene from silacyclobutane was accompanied by an equivalent amount of cyclopropane, which isomerized to propylene at the higher temperature range. Two possible pathways for this extrusion are a cheleotropic elimination requiring concurrent cleavage of both silicon-carbon bonds or a stepwise process initiated by homolysis of a silicon-carbon bond followed by cleavage of the other one within the biradical (eq 3).



(3)

The variation of product ratios with reaction temperature (Table I) permits comment on these mechanisms. As the decomposition temperature was raised from 556 to 697 °C, the amount of SiH$_2$ product **1** increased, albeit slightly, relative to the combined yields of SiCH$_4$ products **2** and **3**. Since the stepwise elimination of SiH$_2$ is expected to have higher activation parameters than a concerted pathway, the enhanced yields of **1** at higher temperature support the radical mechanism.

Especially intriguing and somewhat controversial[9] is the mechanism of formation of the methylsilylene adduct to butadiene.

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(2) Maltsev, A. K.; Khabasheku, V. N.; Nefedov, O. M. *Dokl. Akad. Nauk SSSR* **1979**, *247*, 383.

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(6) All pyrolyses were carried in a seasoned hot zone consisting of a 10-mm i.d. × 30-cm quartz tube. Residence times in the hot zone were on the order of tenths of seconds, and pressures in the hot zone were 1-3 torr. Both residence time and pressure were controlled by a 0.8-mm aperture placed at the end of the pyrolysis chamber.

(7) Jenkins, R. L.; Kedrowski, R. A.; Eliot, L. E.; Tappen, D. C.; Schlyer, D. J.; Ring, M. A. *J. Organomet. Chem.* **1975**, *86*, 347. Previously unreported ^{13}C NMR (neat) for **1** δ 11.2 (t, CH$_2$Si), 130.4 (d, =CH—); for **2** δ -5.6 (q, CH$_3$Si), 14.9 (t, CH$_2$Si), 130.2 (d, =CH—).

(8) ^{1}H NMR (neat) δ 0.54 (2 H, approx sept), 1.02 (2 H, br. s), 1.82 (2 H, br s), 3.59 (2 H, approx q), 5.21 (2 H, br s); ^{13}C NMR (neat) δ 2.9 (t, CH$_2$Si), 4.9 (t, CH$_2$Si), 22.0 (t, CH$_2$), 124.7 (d, —CH=), 130.1 (d, —CH=); *m/e* (relative intensity) 98 (50), 97 (86), 96 (11), 83 (32) 70 (100), 69 (19), 67 (30), 55 (49), 53 (28).

(9) Yoshioka, Y.; Schaefer, H. F. *J. am. Chem. Soc.* **1981**, *103*, 7366. These authors have calculated a barrier of 41 kcal/mol for this isomerization.