$Re(PPh_3)(NO)(CHOH)]^+CF_3CO_2^-$ (**10**)[11] is generated cleanly and quantitatively from **1** and CF_3CO_2H. Complexes containing carbene ligands of the formula $=CHOH$ have not been previously generated, although the intermediacy of such a ligand type in the Fischer–Tropsch process was first considered in 1951.[12] Upon warming, **10** disproportionates to the product mixture quoted above, suggesting that the protonation of **1** is reversible.

The recent study of Cutler[13] bears comment in light of this work. Upon treatment of cationic iron alkoxycarbenes of the formula $[(\eta\text{-}C_5H_5)FeL(CO)(CHOCH_3)]^+PF_6^-$ (**11**) with I^- (1.0–0.5 equiv), equimolar quantities of $[(\eta\text{-}C_5H_5)FeL(CO)_2]^+PF_6$ and $(\eta\text{-}C_5H_5)Fe(CO)_2(CH_2OCH_3)$ were generated. Our data provide additional support for the postulated intermediacy of neutral iron formyls in these reactions, which would rapidly donate hydride to unreacted **11**.

Only one other well-characterized nonbridging methylidene complex, $(\eta\text{-}C_5H_5)_2Ta(CH_3)(CH_2)$ (**12**),[14] has been described in the literature. Whereas the methylidene ligand in **12** is nucleophilic, undergoing ready reaction with $(CH_3)_3SiBr$ and CD_3I, precisely the opposite reactivity is observed with **4** (eq i). Numerous carbene complexes have been observed to form related stable phosphine and amine adducts.[15] As observed with **12**, our ^1H NMR data[5] indicate restricted rotation about the methylidene-metal bond in **4**.

Finally, the facile electrophile-induced disproportionation of formyl **1** may have significant mechanistic relevance to Fischer–Tropsch chemistry.[12] There is substantial hydride mobility associated with homogeneous formyl complexes.[16] Hence, on a Fischer–Tropsch catalyst layered with CO, the generation of low concentrations of catalyst-bound formyls might be accompanied by a similar, electrophile-induced disproportionation.

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(3) Carbonyl cations $[(\eta\text{-}C_5H_5)Re(PPh_3)(NO)(CO)]^+X^-$ were identified by characteristic ^1H NMR resonances (δ 5.85–6.08, s, 5H) and IR absorbances (ν_{CO} 2000–2030 cm^{-1}, ν_{NO} 1760 cm^{-1}).

(4) ^1H NMR spectra were recorded at 200.04 MHz and ^{13}C NMR spectra were recorded at 50.32 MHz on a spectrometer provided by a NSF departmental instrument grant (CHE 76-05926). Probe temperatures were ambient unless noted, and chemical shifts were measured relative to $(CH_3)_4Si$.

(5) ^1H NMR (**4b,** δ, CD_2Cl_2, −70 °C)[4] 15.67 (m, unresolved ABX system, 1 H; at 10 °C: t, $J_{H\text{-}H'} = J_{H\text{-}P} = 4$ Hz), 15.42 (br d, $J_{H'\text{-}H} = 4$, $J_{H'\text{-}P} \leq 1$ Hz), 6.03 ppm (s, 5 H); ^{13}C NMR (**4a,** CD_2Cl_2, −70 °C, gated decoupled) 290.3 (t, $J_{C\text{-}H} = 151$ Hz), 100.5 (d, $J_{C\text{-}H} = 190$ Hz) ppm. Phenyl proton and carbon resonances were obscured by Ph_3CH.

(6) Satisfactory C, H, N, and P analyses were obtained for **5**a, **5b, 6,** and **7.** Spectroscopic data follow.[4] **5a:** ^1H NMR (δ, CD_3CN) 7.58–7.50 (m, 30 H), 4.68 (s, 5 H), 3.23 (m, part of ABXY system, $J_{H\text{-}H'} = 14$, $J_{H\text{-}P} = 11$, $J_{H\text{-}P'} = 8$ Hz, 1 H), 2.68 (m, $J_{H'\text{-}H} = 14$, $J_{H'\text{-}P} = 16$, $J_{H'\text{-}P'} = 1$ Hz, 1 H); ^{13}C NMR (CD_3CN) 91.4, −28.6 (d, $J = 31$ Hz) ppm, and phenyl carbons; IR (cm^{-1}, CH_2Cl_2) ν_{NO} 1650; mp >280 °C. **5b:** ^1H NMR (δ, CD_2Cl_2) 7.51–7.29 (m, 15 H), 5.17 (s, 5 H), 2.15 (m, part of ABXY system, $J = 14, 12, 9$ Hz, 1 H) 2.00–1.20 (m, 18 H + 1 H), 0.94 (t, $J = 7$ Hz, 9 H); ^{13}C NMR (CD_2Cl_2) 90.6, −33.5 (d of d, $J_{C\text{-}P} = 16$, $J_{C\text{-}P'} = 3$ Hz) ppm, and phenyl and butyl carbons; IR (cm^{-1}, CH_2Cl_2) ν_{NO} 1647; mp 229–235 °C. **6:** ^1H NMR (δ, $CDCl_3$) 7.49–7.09 (m, 20 H), 4.74 (d, $J = 1$ Hz, 5 H) 3.50 (d of d, $J = 12, 8$ Hz, 1 H) 2.89 (d of d, $J = 12, 3$ Hz, 1 H); IR (cm^{-1}, CH_2Cl_2) ν_{NO} 1626; mp 180–182 °C. **7:** ^1H NMR (δ, $CDCl_3$) 8.82 (d, $J = 6$ Hz, 2 H) 8.14 (t, $J = 8$ Hz, 1 H), 7.75 (d of d, $J = 6, 8$ Hz, 2 H) 7.53–7.30 (m, 15 H), 5.08 (s, 5 H), 5.81 (d of d, $J = 12, 2$ Hz, 1 H), 5.67 (d of d, $J = 12, 7$ Hz, 1 H); IR (cm^{-1}, CH_2Cl_2) ν_{NO} 1640; mp 180 °C dec.

(7) Anal. ($C_{25}H_{25}NO_2PRe$) C, H, N, P. ^1H NMR (δ, $CDCl_3$)[4] 7.40–7.25 (m, 15 H), 5.04 (d, $J = 0.5$ Hz, 5 H) 5.09 (d of d, $J = 11, 6$ Hz, 1 H), 5.45 (d of d, $J = 11, 2$ Hz, 1 H), 3.16 (s, 3 H); IR (cm^{-1}, CH_2Cl_2) ν_{NO} 1625; mp 175–177 °C.

(8) When this reaction was conducted in toluene, **9** precipitated after stirring overnight. ^1H NMR (δ, CD_2Cl_2)[4] 13.58 (s, 1 H), 7.58–7.18 (m,), 5.85 (s, 5 H), 3.94 (s, 3 H); ^{13}C NMR ($CDCl_3$) 288.4, 96.6, 72.2 ppm, and phenyl carbons; IR (cm^{-1}, CD_2Cl_2) ν_{NO} 1711. After 4 days of vacuum drying, **9** still contained absorbed toluene (10:4 ratio by ^1H NMR). Anal. ($C_{25}H_{24}FNO_5PSRe$ + $0.33C_7H_8$) C, H, N, P.

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(11) ^1H NMR (δ, CD_2Cl_2, −50 °C)[4] 17.80 (br s, 1 H), 14.80 (s, 1 H), 7.64–7.34 (s, 15 H), 5.57 (s, 5 H); ^{13}C NMR (CD_2Cl_2, −60 °C) 277.8, 95.7 ppm, and phenyl, $CF_3CO_2^-$ carbons. In the reaction of **1** with $(CH_3)_3SiCl$ in CD_2Cl_2, a species believed to be the analogous carbene $\{(\eta\text{-}C_5H_5)Re(PPh_3)(NO)[CHOSi(CH_3)_3]\}^+Cl^-$ was formed at −70 °C (δ 15.06 (s, 1 H), 5.91 (s, 5 H); 0.29 (s, 9 H)), along with **3** and $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+Cl^-$.

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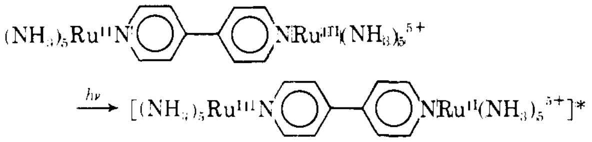
Direct Measurement of the Rate of Intramolecular Electron Transfer in a Diruthenium Mixed-Valence Complex

Sir:

The physical properties of class II mixed-valence ions[1] may be of utility in assessing barriers to electron transfer.[2] Mixed-valence complexes in which the degree of interaction between the two metal sites is moderate (not negligible, but not so large that the sites are equivalent) manifest intervalence transfer absorption[3-6] (e.g., eq 1 for $[(NH_3)_5Ru]_2$-4,4′-bpy^{5+} [7,8]) at energies (E_{op}) which are related by theory to the barriers for thermal electron transfer (E_{th}) within these ions. For the general case in which the two metal coordination spheres are not identical, eq 2 applies:[2]



(1)

$$E_{th,f} = [(E_{op})^2/4(E_{op} - E_0)] - H_{12} \qquad (2)$$

Here $E_{th,f}$ is the barrier for the process endothermic by E_0, the equilibrium energy difference between the two electronic isomers, and H_{12} is the delocalization energy. The intervalence spectra of binuclear species have been extensively characterized,[3-6] and intramolecular electron-transfer rates have been obtained for species which do not manifest intervalence transfer absorption.[9-11] Here we report the rate of intramolecular electron transfer in the mixed-valence ion $(NH_3)_5Ru^{II}pzRu^{III}(edta)^+$ (pz = pyrazine, edta = ethylenediaminetetraacetate) which does exhibit intervalence transfer absorption. As a consequence we are able to test eq 2 directly. Our results suggest a revised model for the electron-transfer process in systems in which the activation barriers arise largely from solvent reorganization.

When $Ru^{II}(NH_3)_5pz^{2+}$ [12] (λ_{max} 472 nm) in pH 5 acetate buffer is mixed with an equivalent amount of yellow $Ru^{III}(Hedta)H_2O\cdot 4H_2O$,[13,14] the pink product I (λ_{max} 520 nm (ϵ_{max} 1.72×10^4 M^{-1} cm^{-1})) results.[15] A class II (trapped-valence) description of the binuclear ion is suggested by its physical properties.[16] No pronounced special stability is associated with

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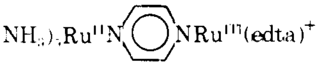
Table I. Results of 527-nm Excitation of Ruthenium(II)–Pyrazine Complexes at 22 ± 2 °C, H_2O, 0.2 M Ionic Strength

entry	complex[a]	λ_{max}, nm	fraction bleached at $t = 0$ ps[b,c]	$10^{-10}k$, s^{-1}
1	$Ru(NH_3)_5pz^{2+}$	472	1.0 ± 0.2	1.3 ± 0.4
2	$Ru(NH_3)_5pzH^{3+}$	529	0.96 ± 0.05	4.0 ± 0.18
3	$(NH_3)_5Ru^{II}pzRu^{II}(edta)$	545	1.15 ± 0.2	0.66 ± 0.05
4	$(NH_3)_5Ru^{II}pzRh^{III}(edta)^+$	529	≥0.9[d]	0.50 ± 0.03
5	$(edta)Ru^{II}pzRu^{II}(edta)^{4-}$	542	0.9 ± 0.1	1.5 ± 0.2
6	$(NH_3)_5RupzRu(NH_3)_5^{5+}$	565	0.19 ± 0.04[e]	>17
7	$(edta)RupzRu(edta)^{3-}$	528	<0.17[e]	>17
8	$(NH_3)_5RupzRu(edta)^+$ (I)	520	0.09 ± 0.03	0.80 ± 0.14

[a] Standard literature methods were used to prepare $[Ru(NH_3)_5pz](TFMS)_2$,[12] $[Rh(NH_3)_5pz](ClO_4)_3$,[12] $Ru(Hedta)H_2O \cdot 4H_2O$,[14] $[(NH_3)_5RupzRu(NH_3)_5]Br_5$.[39] $Rh(Hedta)H_2O$.[40] Entries 3, 4, 5, 7, and 8 were generated in solution at the 10^{-3} to 10^{-2} M level, pH 4.7 with acetate buffer, by mixing equimolar quantities of the starting materials, as follows (product, starting materials, temperature, reaction time): 3, $Ru(NH_3)_5pz^{2+} + Ru(edta)H_2O^0$, 25 °C, 1 h; 4, $Ru(NH_3)_5H_2O^{2+} + Rh(edta)pz^-$, 25 °C, 24 h; 5, $2Ru(edta)H_2O^- + pz + Zn(Hg)$, 25 °C, 1 h (these solutions were diluted to the $0.5–1.0 \times 10^{-3}$ M level to give a final solution with an absorbance of 1.0 (2-mm cell) at 527 nm); 7, equimolar (3.5×10^{-3} M) $[Ru(edta)]_2pz^{2-}$ and $[Ru(edta)]_2pz^{4-}$ were diluted with 10^{-3} M $Ru(edta)H_2O^-$ solution to give an absorbance of 1.0 (2-mm cell) at 527 nm; 8, $Ru(NH_3)_5pz^{2+} + Ru(edta)H_2O^-$, 5×10^{-4} M final. Rh(Hedta)pz was prepared by heating an aqueous solution of $Rh(Hedta)H_2O$ and pyrazine for 1 h on a steam bath.[41] [b] The fraction bleached is defined as ΔA at $t = 0$ divided by the absorbance before the flash determined on a Cary 17. The absorbance changes (monitored between 560 and 600 nm) were typically 0.1 to 0.5. At "$t = 0$" ps the interrogation and excitation pulses overlap in time. [c] The molar absorptivities of the complexes ranged from 0.3 to 2.9×10^4 M^{-1} cm^{-1} at 527 nm. Consequently the light intensity was sufficient to excite ≥90% of the sample in all cases. [d] Large errors are associated with this value because the absorbance of the solution in the monitoring region was low (0.15) and stray light was consequently more of a problem. [e] No net bleaching was observable after 10 ps. The values measured at "$t = 0$" ps reflect changes occurring *during* the pulse.

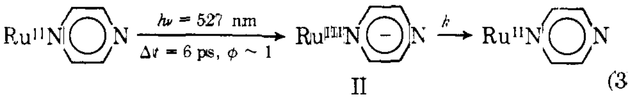


I

the mixed-valence oxidation state; the affinity of $Ru^{III}(edta)H_2O^-$ for $(NH_3)_5Rupz^{2+}$ ($K = 3 \times 10^4$ M^{-1}) differs little from its affinity for pyrazine itself ($K = 2.0 \times 10^4$ M^{-1} [13]), and I is actually more readily oxidized ($E_{1/2} = 0.56$ V) than $(NH_3)_5Ru^{II}pzRh^{III}(edta)^+$ ($E_{1/2} = 0.61$ V) in which no resonance stabilization is feasible. In addition, the characteristics of the near-infrared transition are compatible with a trapped-valence assignment: from the band position (1020 nm, 9.8 kK), molar absorptivity (3×10^2 M^{-1} cm^{-1}), and half width (~3.7 kK), a value of 0.8 kcal mol^{-1} is calculated for H_{12}.[1,2,16]

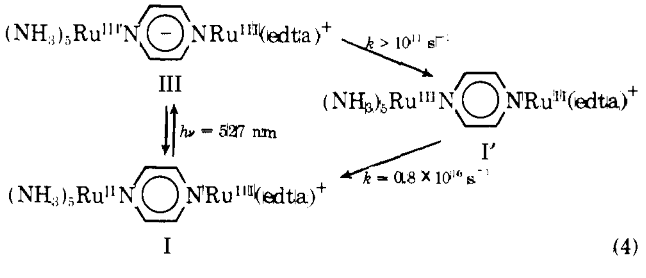
Aqueous solutions of $(NH_3)_5Ru^{II}pzRu^{III}(edta)^+$ (~5×10^{-4} M, 2-mm cell, 0.01 M acetate buffer, pH 5, $\mu = 0.2$ M KCF_3SO_3) and other complexes containing Ru(II) and pyrazine were subjected to flash photolysis. For studies of the 10^{-11}- to 10^{-9}-s time domain the technique of picosecond spectroscopy[17-21] was exploited: a single pulse (~8-ps full width at half height) from a neodymium glass laser was frequency doubled to produce a 3- to 4-mJ photolysis pulse at 527 nm. A white light pulse[22-26] of ~8-ps duration was produced by focussing the undoubled laser light into a cell of carbon tetrachloride, split into two beams, and used to monitor absorbance changes in the range 550–850 nm.[27] One beam traversed the excited region of the sample; the other was used to correct for shot-to-shot fluctuations in the intensity of the white light. For all of the complexes excited with 527-nm light, a transient bleaching of the ground-state absorbance beyond 550 nm resulted from the excitation pulse. The return of ground-state absorption was generally followed with a Vidicon detector coupled to a 0.25-m J-Y spectrograph. The magnitudes of the bleaching and the rate constants for the return of ground state absorption are presented in Table I. By contrast, no transient was detectable upon flash photolysis of I (entry 8) using 1054-nm laser light (~22 mJ/pulse).

The first five complexes in Table I contain Ru(II) and pyrazine, but no Ru(III). For all five, 527-nm excitation produces quantitative bleaching of the ground state immediately after the pulse. Afterward the ground-state absorbance is restored exponentially with a rate constant ranging from 5×10^9 to 4×10^{10} s^{-1} depending on the complex. The transient is identified with the metal-to-ligand charge transfer (MLCT) excited state II (eq 3) on the basis of several considerations. First, 527-nm light absorption corresponds to excitation in the MLCT band.[12,28] A different state is likely to be populated from the MLCT state only if the second state is lower in energy than the MLCT state. Malouf and Ford[29] have shown that, for $Ru(NH_3)_5L^{2+}$ (L an aromatic N heterocycle), the MLCT states are the lowest energy states when λ_{max} for the MLCT transition lies beyond ~480 nm. With the exception of $Ru(NH_3)_5pz^{2+}$, all of the complexes studied here have λ_{max} ≥520 nm. Furthermore, with the exception of $Ru(NH_3)_5pz^{2+}$, no photoaquation ($\phi < 10^{-3}$) results from 527-nm excitation; this is consistent with the ligand field states lying at higher energy.[29] In addition, as is expected for the MLCT state II, no intense ($\epsilon > 10^3$ M^{-1} cm^{-1}) excited-state absorption is detected in the region 300–500 nm[30] or beyond 550 nm.



(3)

Equation 3 is also expected to provide a model for the photophysical behavior of the symmetrical mixed-valence ions[31] $[(NH_3)_5Ru]_2pz^{5+}$ and $[Ru(edta)]_2pz^{3-}$ (entries 6 and 7 in Table I), but for these the MLCT states are found to be extraordinarily short-lived—no transients remain after ~10 ps. The behavior of the symmetric mixed-valence ion I (entry 8) is, however, unique. The fraction of ground-state bleaching after the pulse is ~1/10 of that for the first five entries in the table; yet the pre-flash absorbance is restored at a relatively slow rate. We propose that the electronic isomer I′ has been obtained by decay of III, the MLCT state of I and I′ (eq 4).



(4)

The decay of the MLCT state III to produce I′ rather than I is favored by energy gap considerations.[32] The quantum yield of I′ cannot be obtained from these experiments alone, but the fact that the molar absorptivities and spectral maxima of $(NH_3)_5Ru^{II}pz$ and $(edta)Ru^{II}pz$ chromophores generally differ by less than ~20%[33] suggests that the observed fractional bleaching of 0.09 ± 0.02 at 560 nm corresponds to a high overall yield of I′.

The rate constant measured here for regeneration of I may be compared with that calculated for the back intramolecular electron transfer, I′ → I, by using eq 2, $E_{th,r}$ (the barrier for this back electron transfer) $= (E_0 - E_{th,f})$, and the values $E_{op} = 1.21$ eV, $H_{12} = 0.035$ eV. E_0 is estimated as 0.3 eV from the difference in the reduction potentials of $(NH_3)_5Ru^{III}pz\text{-}Rh^{III}(edta)^{2+}$ and $(NH_3)_5Rh^{III}pzRu^{III}(edta)^{2+}$ ($E_{1/2} = 0.67$ and 0.37 V, respectively, 25 °C, H_2O, $\mu = 0.2$ M). The barrier $E_{th,r}$ is thus estimated to be 0.065 eV. Assuming that $T\Delta S^{\ddagger} = 0$[38] and that $k_{calcd} = (kT/h)\exp(-E_{th,r}/RT)$, k_{calcd} is $5 \times 10^{11}\ s^{-1}$ which is about 50 times greater than the observed rate constant. Although the agreement between the observed and calculated rate constants must be considered satisfactory, the results for excitation of I with 1054-nm radiation raise several fundamental questions. The quantum yield for the formation of the thermally equilibrated electronic isomer I′ following excitation in the intervalence transfer band is <0.1 (assuming that it is 0.5 for 527-nm excitation). Similarly, intervalence transfer excitation (1060 nm) of the ion pair $Fe^{II}(CN)_6^{4-}/Ru^{III}(NH_3)_5py^{3+}$ [34] (ϵ_{1060} 30 $M^{-1}\ cm^{-1}$) yields $Fe^{III}(CN)_6^{3-}/Ru^{II}(NH_3)_5py^{2+}$ with a quantum yield of only 0.06 ± 0.03.[35] The low quantum yields for the formation of the electronic isomers in these two systems require that the relaxation rates of the Franck–Condon intervalence-transfer states to the (original) ground states exceed the rates of formation of the barriers to reverse electron transfer. For both systems this barrier arises largely from differences in solvent polarization at the two metal sites.[8,36] The time required to establish the solvent barrier is determined by the dielectric relaxation frequency of water ($\sim 10^{11}\ s^{-1}$ [37]). Since this frequency is 10–100 times lower than metal–ligand (and intraligand) vibration frequencies, the Franck–Condon states could relax to the original ground states via the relatively high-frequency inner-sphere modes before the change in solvent polarization can occur. As a result, the solvent barrier to the reverse electron transfer may never be established.[42] The difference between the characteristic times for solvent and inner-sphere relaxations (and for electron transfer) may have another important consequence: the frequency factor for the thermal electron transfer might in certain circumstances be determined by the dynamics of the solvent reorganization. In this connection it could be significant that the agreement between the observed and calculated rate constants for the back electron transfer is considerably improved if the dielectric relaxation frequency for water ($10^{11}\ s^{-1}$ [37])[43] rather than kT/h ($62 \times 10^{11}\ s^{-1}$) is used as the preexponential factor. Further studies aimed at ascertaining the generality of this result as well as the role of E_0, bridging ligand, temperature, solvent, etc., are currently in progress in this laboratory.

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(30) Observations were made during the 530-nm, 20-ns excitation pulse from a frequency doubled Nd laser. See ref 18 for a description of the technique.
(31) The electrochemical and spectral characteristics of $[(edta)Ru]_2pz^{3-}$ indicate that the ion is probably class II: $E_{1/2} \sim 0.18$, 0.32 V; λ_{max} 528 nm (ϵ $2.5 \times 10^4\ M^{-1}\ cm^{-1}$), 970 ($2.4 \times 10^2\ M^{-1}\ cm^{-1}$); $\Delta\nu_{1/2}$ 4.7 kK. The electronic structure of $[(NH_3)_5Ru]_2pz^{5+}$ has, however, been the subject of much debate. See for example: Beattie, J. K.; Hush, N. S.; Taylor, P. R. *Inorg. Chem.* **1976,** *15*, 992 and references cited therein. Bunker, B. A.; Drago, R. S.; Hendrickson, D. N.; Kessell, S. L. *J. Am. Chem. Soc.* **1978,** *100*, 3805 and references cited therein.
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(33) Consider the following data (complex, λ_{max} in nm (ϵ_{max} in $M^{-1}\ cm^{-1}$)): $Ru(NH_3)_5pz^{2+}$, 472, 1.4×10^4; $Ru(edta)pz^{2-}$, 463, 1.2×10^4; $(NH_3)_5RupzRh(NH_3)_5^{5+}$, 528, 1.8×10^4; $(edta)RupzRh(NH_3)_5^+$, 533, 1.8×10^4; $(NH_3)_5RupzRh(edta)^+$, 529, 1.9×10^4; $(edta)RupzRh(edta)^{3-}$, 531, 2.2×10^4.
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(38) A more correct description takes into account that E_{op} and H_{12} are enthalpies while a reduction potential difference is a free energy $\Delta G_f°$. When it is assumed that $T\Delta S_f°$ between I and I′ is at most 0.1 eV, use of the following equation gives 0.076 eV for $\Delta G_{th,r}^{\ddagger}$ and $3.4 \times 10^{11}\ s^{-1}$ as the calculated rate constant when $\Delta G_f° = 0.3$ eV.

$$\Delta G_{th,r}^{\ddagger} = \frac{(E_{op})^2}{4(E_{op} - \Delta G_f° - T\Delta S_f°)} - H_{12} - \frac{T\Delta S_f°}{2} - \Delta G_f°$$

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(42) In terms of this model, because of its finite lifetime the relatively symmetrical MLCT state could equilibrate and then decay with about equal probability to the ground state or its electronic isomer.
(43) A more detailed treatment should include the dispersion in the frequencies of the medium.

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