Chemical Society, and to the National Institutes of Health (GM 15431), DHEW, for partial support of this work.

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(14) The distilled material showed three peaks on GLC (1/8 in. × 6 ft, 3% OV-17, 160 °C, 25 mL/min; retention times 7.25, 8.00, and 9.50 min) in a ratio of 10.3:86.9:2.8. These were assigned structures **4, 2**, and **11**, respectively,
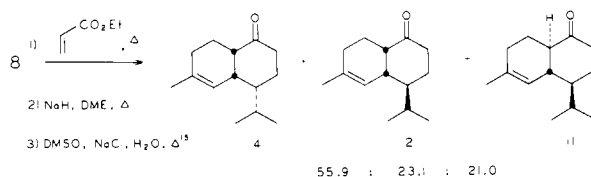
on the basis of the following: The three gave quite similar but distinct mass spectra. A comparison sample (which should have roughly equal isopropyl isomers from the initial addition) was prepared by a modification of the method of Vig.[6] This procedure gave the same three GLC peaks, having superimposable mass spectra, in the ratio indicated. Finally, refluxing the initial mixture from the oxidation of **9** in methanolic sodium methoxide gave again the same three peaks, this time in a ratio of 10.1:47.2:42.7.

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Electron-Transfer Reactions in the "Abnormal" Free-Energy Region

Sir:

For an outer-sphere electron-transfer reaction, the rate constant can be written as

$$k = \nu_{et} K \exp[-(\Delta G^*/RT)] \tag{1}$$

where ν_{et} is the frequency factor for electron transfer within an ion pair or association complex of the reactants and K is the formation constant for the association complex. From their classical treatments of ΔG^*, Marcus[1] and Hush[2] have derived eq 2, where ΔG is the free-energy change on electron transfer within the association complex and λ is the optical or vertical vibrational barrier to electron transfer. Combining eq 1 and 2 gives eq 3:

$$\Delta G^* = \frac{\lambda}{4}\left(1 + \frac{\Delta G}{\lambda}\right)^2 \tag{2}$$

$$k = \nu_{et} K \exp\left(\left[\frac{-\lambda}{4RT}\left(1 + \frac{\Delta G}{\lambda}\right)^2\right]\right) \tag{3}$$

This has been tested repeatedly in different forms (e.g., see ref 3 and 4). Equation 3 successfully predicts an increase in k as

$-\Delta G$ increases and approaches λ, but makes the remarkable prediction that, for reactions in the "abnormal" or "inverted" free-energy region where $-\Delta G > \lambda$, k should decrease as ΔG becomes even more favorable.

To date, studies of reactions in the abnormal free-energy region have been based on excited-state quenching experiments.[6-8] The results show that there is at best a slight decrease in k as ΔG becomes even more favorable in contrast to the prediction made by eq 3. A second experimental approach to the problem is the use of the flash photolysis technique, where a reaction in the abnormal free energy can be induced by an initial excited-state quenching step (eq 4, 5).[9]
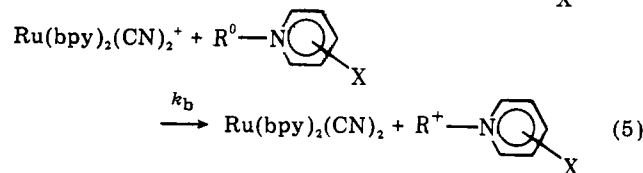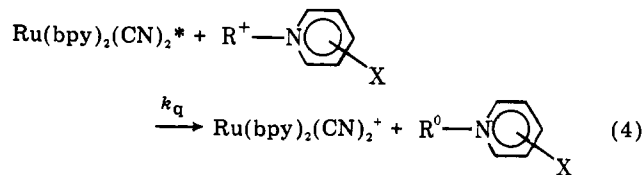

We have measured both quenching (k_q, eq 4)[10] and back electron-transfer (k_b, eq 5)[11] rate constants in acetonitrile ($I = 2.0 \times 10^{-3}$–5.0×10^{-1} M using $[NEt_4^+](ClO_4^-))$[12] at room temperature for a series of reactions involving the dicyano complexes $Ru(bpy)_2(CN)_2$ (bpy is 2,2'-bipyridine) and $Ru(phen)_2(CN)_2$ (phen is 1,10-phenanthroline) and the pyridinium type ions:
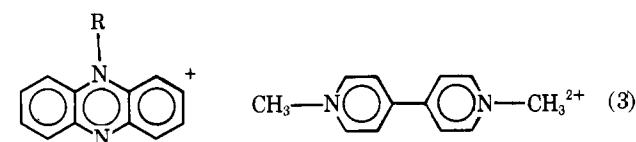
R = CH₃ (1), C₂H₅ (2)
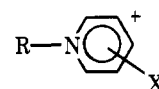
R = CH_3; X = 4-CN (4), 4-C(=O)OCH₃ (5), H (14), 3-C(=O)NH₂ (11), 4-C(=O)NH₂ (8)
R = C_2H_5; X = 4-C(=O)OCH₃ (6), 4-C(=O)NH₂ (7), 3-C(=O)NH₂ (10), H (13)
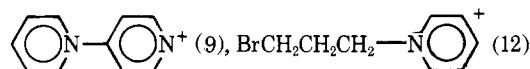
The numbers in parentheses identify the quenchers used to obtain the data shown in Figure 1.

The reactions involve a series of structurally related reactants, where ΔG varies widely but λ, K, and ν_{et} are expected to be nearly the same. The reactions are also attractive from the interpretive point of view because they are free of electrostatic effects arising from charge–charge interactions (eq 4, 5).

Values for k_q referred to as "quenching" in Figure 1 were obtained by luminescence quenching[10] and for k_b by flash photolysis. The data are shown in Figure 1 as a plot of $RT \ln k_{obsd}$ (k_q or k_b) against ΔG. The ΔG values were calculated from redox potentials for the couples involved.[13]

Assuming that $\nu_{et} K$ and λ are reasonably constant for the series of quenching reactions, eq 3 in logarithmic form

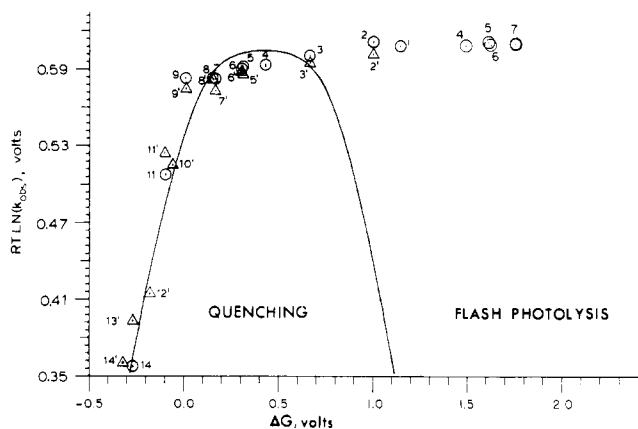$$RT \ln k = RT \ln \nu_{et} K - \frac{\lambda}{4}\left(1 + \frac{\Delta G}{\lambda}\right)^2 \tag{3a}$$

Figure. 1 Plot of $RT \ln K_{obsd}$ vs. ΔG for quenching and flash photolysis reactions involving $RuL_2(CN)_2^*$ ($\odot$, L = bpy; $\triangle$, L = phen) and various pyridinium ions. The numbering scheme is the same as that given in the text. The curved line represents calculated values of $RT \ln k_{obsd}$ using eq 3a including corrections for diffusional effects, eq 6. The values $\nu_{et}K = 8.2 \times 10^{10} \ M^{-1} s^{-1}$, $\lambda = 9.7$ kcal/mol, and $k_D = 2.1 \times 10^{10} \ M^{-1} s^{-1}$ were used in the calculations.
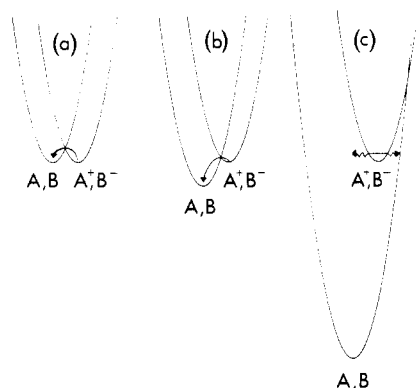

Figure 2. Potential energy diagrams for an electron-transfer reaction, $A^+, B^- \rightarrow A, B$, where (a) $\Delta G = 0$; (b) $\delta G < 0$; $-\Delta G < \lambda$; (c) $\Delta G < 0$; $-\Delta G > \lambda$.

correctly predicts the observed increase and flattening in $RT \ln k_{obsd}$ as $-\Delta G$ increases in the normal free-energy region where $-\Delta G < \lambda$. By taking into account diffusional effects (eq 6),[14] the approach of k_{obsd} to the diffusion-controlled limit k_D ($2.1 \pm 0.1 \times 10^{10} \ M^{-1} s^{-1}$; $RT \ln k_D = 0.61$ V)[15] as $-\Delta G$ approaches λ is also predicted by eq 3a.

$$\frac{1}{k_{obsd}} = \frac{1}{k_D} + \frac{1}{k} \qquad (6)$$

Of more interest here are the data for the back electron-transfer reactions where $-\Delta G > \lambda$, since they fall in the abnormal free-energy region. From the data in Figure 1, it is apparent that there is no evidence for the decrease in k predicted by eq 3. The predicted decrease is shown in the figure by the solid line, which was calculated from eq 3a assuming that $\nu_{et}K = 8.2 \times 10^{10} \ M^{-1} s^{-1}$ and $\lambda = 9.7$ kcal/mol. In calculating the line, diffusional effects were included using eq 6.

The failure of eq 2 to predict the lack of a free-energy dependence in the abnormal free-energy region is because the equation is based on a classical treatment for the vibrations involved. Full quantum mechanical treatments have been given for electron-transfer processes.[20] From those treatments, in the normal free-energy region, ΔG^* and the temperature dependence of k arise in a natural, easily interpretable way. Thermal activation to higher vibrational levels is necessary (Figure 2a,b), because there the distribution of possible nuclear configurations in the vibrational states includes configurations

that are appropriate for the products in isoenergetic vibrational levels. That is to say that vibrational overlap between wave functions for reactants and products is greatly improved. In the high-temperature limit, Duke[21] and others[20e,f] have shown that the quantum mechanical treatment leads to eq 2.

In the so-called "abnormal free-energy region", the reactant vibrational manifold is within the product manifold (Figure 2c). Electron transfer between reactants to give products involves a transition between different electronic states. In fact, the criterion that $-\Delta G > \lambda$ is simply a statement that the electron-transfer process has changed from a thermal relaxation (Figure 2a,b) to the radiationless decay of an outer-sphere charge-transfer excited state (Figure 2c). The classical picture, which leads to eq 2, still predicts that electron transfer occurs following thermal excitation to the intersection region between classical potential energy surfaces. However, quantum mechanically there is no a priori reason to expect that activation to the intersection region is necessary. Rather, the critical issues become those in excited-state radiationless decay processes, namely the electronic coupling matrix element, the density of acceptor vibrational levels, and the magnitude of the vibrational overlap integrals involved.[22]

For the outer-sphere charge-transfer decay processes that have been investigated to date, the absence of a dependence on ΔG shows that the classical treatment is incorrect. From the quantum mechanical viewpoint, since $\Delta G^* \simeq 0$, transition probabilities from equilibrium or near-equilibrium vibrational levels of the reactants must be high, and extensive thermal activation to higher vibrational levels is unnecessary.

The conclusions reached here are of obvious general importance, since they pointed out, for example, that recent attempts to use eq 2 in discussing slight rate constant decreases with increasing $-\Delta G$ for outer-sphere excited-state processes[7] or variations in electron-transfer quenching rate constants with ΔG[23] are misguided. In fact, there is no real theoretical or experimental basis for expecting that eq 2 should apply to either problem.

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(10) k_q values were obtained by luminescence quenching experiments. Plots of I_0/I vs. [Q] were linear, as predicted by the Stern–Volmer equation where I and I_0 are the luminescence intensities in the presence and absence of the quencher Q. k_q values were calculated from the slopes of the plots using $\tau_0 = 1260$ ns for $Ru(phen)_2(CN)_2^*$ and $\tau_0 = 253$ ns for $Ru(bpy)_2(CN)_2^*$, which were measured independently. For the reactions cited, there was no spectral evidence either for ground- or excited-state (exciplex) complex formation.
(11) Under the conditions used for the flash photolysis experiments, sufficient quencher was present in the solutions, a few millimoles/liter, that the excitation and quenching (eq 4) steps occur during the flash. Following the flash, absorbance changes (ΔA) were observed as a function of time. As expected from eq 4 and 5, second-order, equal concentration kinetic plots of $1/\Delta A$ vs. t were linear for at least 2–3 half-lives. k_b was evaluated from the slopes of the plots using known extinction coefficient changes.
(12) Ionic strength studies on the reaction between $Ru(bpy)_2(CN)_2^+$ and $Et^0NC_6H_4C(=O)OCH_3$ show the expected absence of a significant variation of k_b with I.

(13) Potentials for the excited-state couples Ru(bpy)$_2$(CN)$_2$$^{+/0*}$ and Ru-(phen)$_2$(CN)$^{+/0*}$ were estimated by subtracting the experimental emission energies (1.86 and 1.88 V) plus 0.05 V from the ground-state (Ru(III)/Ru(II)) potentials (0.83 and 0.84 V). The factor of 0.05 V has been estimated to be the difference between the emission energy and the free-energy content of the thermally equilibrated excited state for Ru(bpy)$_3$$^{2+}$*.[4]

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(19) Given the energies involved (ref 13), ΔG for even the most highly favored reactions are insufficient to repopulate the MLCT excited states so that complications from the reactions

$$R^0—N\bigcirc X + Ru^{III}(bpy)_2(CN)_2^+ \longrightarrow R^+—N\bigcirc X + Ru(bpy)_2(CN)_2^*$$
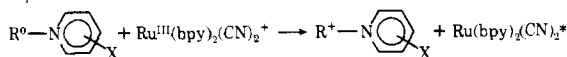
do not exist.

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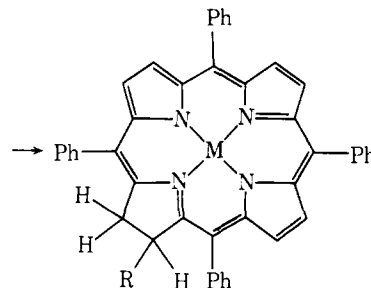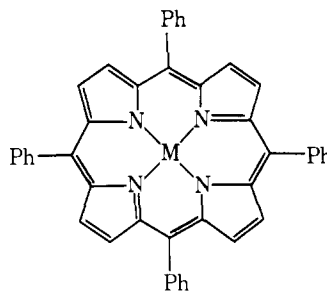
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1, M = Pd; R = H
3, M = Pd; R = CH$_2$N(–CH$_3$)C$_6$H$_5$

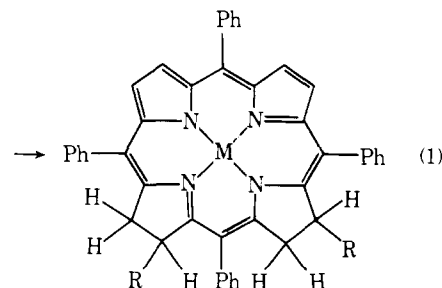2, M = Pd; R = H
4, M = Pd; R = CH$_2$N(–CH$_3$)C$_6$H$_5$

Exciplex Formation from Transition-Metal Complexes. Luminescent Nonpolar Exciplexes from Palladium(II) Porphyrin Triplets and N,N-Dimethylaniline

Sir:

Both photoredox reactions and exciplex emission have been observed upon irradiation of various chromophores in the presence of amines.[1–8] While exciplex emission has been observed for a variety of organic substrates, it has not been generally detected with transition-metal complexes,[9,10] even though the latter frequently undergo photoreaction with amines and other substrates that give luminescent exciplexes with aromatic hydrocarbons.[11–15] One group of reactions that might be anticipated to involve exciplex intermediates is the photoreduction of metalloporphyrins. This reaction, which has been observed for a variety of different metal complexes,[14–17] generally involves the consecutive conversion of the porphyrin to chlorin and isobacteriochlorin complexes (eq 1) under irradiation in the presence of a variety of reducing agents. In recent investigations we have examined photoreactions of the platinum(II) and palladium porphyrins.[18] These complexes show very weak fluorescence and prominent phosphorescence in fluid media at room temperature, and the long triplet lifetimes, particularly for the palladium complexes,[18–20] permit the observation in several cases of relatively slow and energetically uphill excited-state reactions.[18] We felt that these properties should make these complexes especially useful for a study of metalloporphyrin excited-state interactions with amines and other reductants. In the present paper we report results that indicate the formation of luminescent exciplexes between amines and palladium porphyrin triplets. Our results indicate that the exciplex has little charge-transfer character and strongly resembles the uncomplexed porphyrin triplet in both lifetime and emission spectrum. The results observed here with luminescent triplets are apparently related to those obtained previously for nonemitting metalloporphyrin triplets with electron acceptors.[21,22]

Palladium(II) porphyrin complexes were prepared as previously described.[18,23] Our study has included several different porphyrins (e.g., octaethylporphyrin, $\alpha,\beta,\gamma,\delta$-mesotetraphenylporphine (TPP), and mesotetra($\alpha,\alpha,\alpha,\alpha$-o-hexadecylamidophenylporphine)), as well as a number of potential donors (triethylamine, N,N-dimethylaniline (DMA), and SnCl$_2$·2H$_2$O); however, the present report will deal only with the system PdTPP–DMA, which shows typical behavior and has been studied in greatest detail. Irradiation of degassed solutions of PdTPP in the presence of 0.5–5 M DMA in a number of solvents (e.g., benzene, pyridine, acetone, 2-propanol, or isobutyronitrile) with light absorbed only by the porphyrin leads to inefficient ($\phi \simeq 0.001$ at 3.9 M DMA) formation of reductive adducts 3 and 4. In addition to photoadduct formation, we find that DMA produces changes in