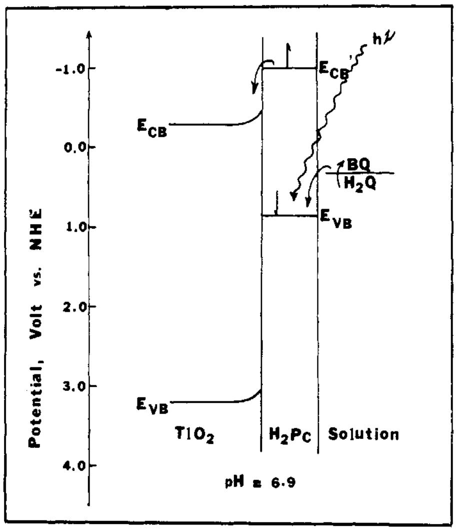

Figure 2. Schematic diagram for the electron transfer at H_2Pc on TiO_2. E_{CB} and E_{VB} denote the potentials of the conduction band edge and the valence band edge of TiO_2. E_{CB}' and E_{VB}' are the corresponding potentials for H_2Pc. Redox potential for *p*-hydroquinone (H_2Q)/*p*-benzoquinone (BQ) is shown on the right.

The photocatalytic activity of suspended phthalocyanine-coated TiO_2 powder can be correlated with the photoelectrochemical behavior of n-type TiO_2 (rutile) single-crystal electrodes covered with phthalocyanine thin films. As shown in Figure 1, the photoinduced oxidation of hydroquinone on an illuminated H_2Pc-coated TiO_2 electrode takes place at more negative potentials than the reduction of oxygen on the TiO_2 electrode. Thus, the photooxidation of hydroquinone on phthalocyanine sites and the reduction of oxygen on TiO_2 sites can take place simultaneously on the same particle. As shown by the energy level scheme in Figure 2, irradiation of an H_2Pc-coated TiO_2 particle with light of energy smaller than the band gap of TiO_2 but greater than the band gap of H_2Pc (~2 eV)[16] causes excitation of an electron to the conduction band of H_2Pc leaving a hole in the valence band. The photogenerated holes are sufficiently energetic (~0.8 V vs. NHE)[17] to oxidize hydroquinone while the photogenerated electrons are injected into the conduction band of TiO_2 leading to the reduction of oxygen.

Note that the photogenerated holes formed by the excitation of phthalocyanines are insufficiently energetic to oxidize H_2O or Cl^-. In the absence of hydroquinone or other reducing agents, the sensitized photocurrent showed a peak around −0.30 V vs. SCE (see curve c in Figure 1) which decreased with time. This photocurrent is attributable to the photooxidation of phthalocyanines, which in the absence of reducing agents remains in the oxidized state. The addition of hydroquinone which acts as a "supersensitizer" is required to obtain a continuous current. The quantum efficiency for the photooxidation of hydroquinone at 632.8 nm under light intensity of ~50 mW/cm^2 was estimated to be ~0.1%. It is interesting to notice that, different from the photocurrent peak shown in Figure 1c for the H_2Pc-coated electrode, the peak photocurrent on the bare TiO_2 electrodes (d) was time independent and was located at a slightly more positive potential (−0.22 V vs. SCE). The origin of this peak is not clear, but it probably involves the surface states of TiO_2.

The experiments described here demonstrate the feasibility of sensitized photoassisted redox reactions with phthalocyanine-coated semiconductor powders. Sensitized heterogeneous photocatalytic and photoelectrosynthetic processes employing other semiconducting substrate powders and other phthalocyanines are currently under investigation in this laboratory.[18]

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Free-Energy Relationships for Electron-Transfer Processes

Sir:

Following the absolute reaction-rate theory, the rate constant of an outer-sphere electron-transfer (ET) reaction (eq 1) is given in eq 2 where A is the frequency factor and $\Delta G^{\ddagger}$ is the free energy of activation. At least three different relationships between the free energy of activation, $\Delta G^{\ddagger}$, and the standard free-energy change, ΔG, are currently used to discuss the results obtained in homogeneous series of ET reactions.

$$M + N \xrightarrow{k} M^+ + N^- \quad (1)$$

$$k = Ae^{-\Delta G^{\ddagger}/RT} \quad (2)$$

(i) One is the Marcus equation[1] (eq 3) where $\Delta G^{\ddagger}(0)$ is the so-called "intrinsic barrier", i.e., the free energy of activation for a reaction with $\Delta G = 0$:

$$\Delta G^{\ddagger} = \Delta G^{\ddagger}(0)[1 + (\Delta G/4\Delta G^{\ddagger}(0))]^2 \quad (3)$$

(ii) There are linear free-energy relationships (eq 4) of the type discussed by Brønsted and Pedersen[2] and by Polanyi et al.,[3] where α and β are two empirical parameters:

$$\Delta G^{\ddagger} = \alpha\Delta G + \beta \quad (4)$$

(iii) The third is the empirical relationship (eq 5) first proposed by Rehm and Weller (RW),[4] where $\Delta G^{\ddagger}(0)$ has the same meaning as in eq 3:

$$\Delta G^{\ddagger} = \frac{\Delta G}{2} + \left\{\left(\frac{\Delta G}{2}\right)^2 + [\Delta G^{\ddagger}(0)]^2\right\}^{1/2} \quad (5)$$

It is the purpose of this letter to discuss some aspects of these relationships and to suggest the use of another one first derived by Marcus[5] for atom- and proton-transfer reactions and more recently obtained by Agmon and Levine[6] on the basis of a

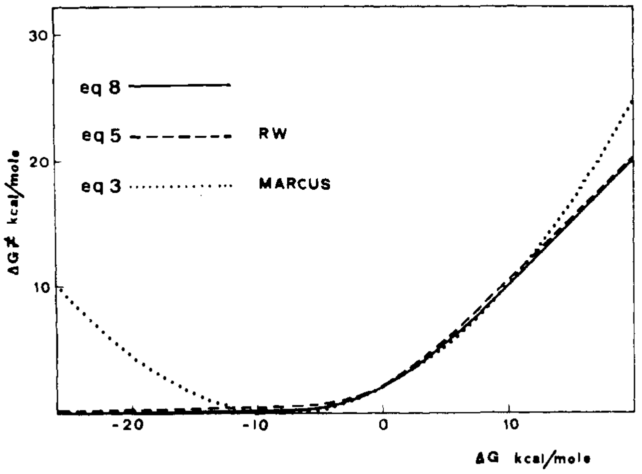

Figure 1. Graphical representation of the free-energy relationships for ET processes: full line, eq 8; broken line, eq 5 (RW function); dotted line, eq 3 (Marcus function). Calculation performed with $\Delta G^{\ddagger}(0) = 2$ kcal/mol.

thermodynamic-like treatment of concerted reaction kinetics.

The Marcus relationship (eq 3) is the result of an adiabatic theory of ET processes[1,7] which has been successfully used to rationalize the kinetic data on many thermal ET reactions.[1,7-10] A graphical representation of eq 3 is shown in Figure 1. An important feature of this relationship is the large $\Delta G^{\ddagger}$ predicted for highly exoergonic reactions (Marcus inverted region, $\Delta G < -4\Delta G^{\ddagger}(0)$). Experimental evidence for or against such an inverted region usually cannot be obtained when both the reactants of the ET process are in their ground state because ΔG is not sufficiently negative. However, the use of electronically excited species as reactants has recently allowed exploration of the inverted region in a systematic way,[4,11-19] showing that the decrease in reaction rate predicted by eq 3 for highly exoergonic reactions does not take place. Tentatively, alternate pathways through exciplexes or low-lying electronically excited states of the products may be invoked to accommodate these results within the frame of the Marcus theory.[4] However, such alternate paths can be ruled out in several cases.[20] Thus, experimentalists are looking for empirical but more satisfactory relationships (see below) and theoreticians are trying to revise the Marcus theory or to explore other types of theoretical approaches.[22-28]

In recent papers[29-33] on the quenching of excited states by inorganic species, more or less linear plots of the logarithm of the quenching constant vs. ΔG (or some related quantity) are reported and taken as an indication of an ET quenching mechanism.[34] In particular, Shizuka et al.[32] have discussed the quenching of aromatic fluorescence by inorganic anions on the basis of eq 4. From a straight line drawn through experimental points in the range -1 eV $< \Delta G <$ 0.7 eV, the values 0.114 and 0.120 eV were obtained for α and β. We would like to remark that in most of that ΔG range such values would imply $\Delta G^{\ddagger} < \Delta G$, which is nonsense. More generally, it should be noted that eq 4 has a very bad behavior for high positive or negative ΔG values, as $\Delta G^{\ddagger}$ should tend toward a fraction of ΔG when ΔG becomes large and positive and should reach sharply zero for $\Delta G = -\beta/\alpha$. That eq 4 has severe limitations for a quantitative and accurate discussion of free-energy relationships over a sufficiently broad range of ΔG changes is well known.[35-37] As shown later, these limitations are expected to be particularly stringent for processes having relatively low intrinsic barriers, such as the outer-sphere ET reactions. Thus, in spite of the recent claim of Shizuka et al.[33] that eq 4 can also be applied to the ET quenching systems previously reported by RW[4] and Vogelmann et al.,[11] we strongly disfavor the use of this equation. It should also be realized that a "linear" free-energy relationship cannot be taken as a proof of an ET quenching mechanism since the quenching via an exciplex with greater or lesser charge-transfer character is expected to give a similar result.[38-40] As shown later, complete ET can only give rise to a linear relationship with $\alpha = 1$ and $\beta = 0$, in the limit of high and positve ΔG values.[41]

Equation 5 was first proposed by RW[4] to account for their results on the ET quenching of aromatic hydrocarbon fluorescence. Since then, this relationship has been found to be at least qualitatively obeyed by all the systems studied and has thus gained wide acceptance.[4,11-18] This equation has also been recently used in the extension of the Marcus formalism to energy-transfer processes.[19,42] The key features of the RW relationship follow (Figure 1): (i) for an isoergonic reaction, there is an activation energy equal to the intrinsic barrier $\Delta G^{\ddagger}(0)$ of the Marcus theory; (ii) $\Delta G^{\ddagger}$ tends asymptotically toward ΔG for highly endoergonic reactions; (iii) $\Delta G^{\ddagger}$ tends asymptotycally toward zero for highly exoergonic reactions. In practice (Figure 1), eq 5 behaves very similarly to eq 3 for $|\Delta G| \leqslant 4\Delta G^{\ddagger}(0)$, but it differs from eq 3 for very negative ΔG where it does not predict the inverted region and for very positive ΔG where it predicts a linear instead of a quadratic dependence of $\Delta G^{\ddagger}$ on ΔG.

Since the origin of the RW equation is completely empirical,[4] any other function showing the same general features (points i to iii above) and descending from a theoretical treatment would be more acceptable. This is the case of the free-energy relationship that was first obtained by Marcus[5] for atom- and proton-transfer reactions on the basis of the BEBO method. The same relationship has been recently obtained by Agmon and Levine[6,43] from a thermodynamic-like treatment of concerted reaction kinetics. Such a treatment is based on the assumption that the standard free-energy profile of a concerted reaction, in which the change from reactants to products is represented by a progress variable n going from 0 to 1, is determined by two additive terms:[44]

$$G(n) = n\Delta G + [\Delta G^{\ddagger}(0)/\ln 2]M(n) \qquad (6)$$

For ET processes, n can be related to the fraction of charge transfer along the reaction coordinate.[7,9,36,37] The first term in eq 6 is simply a linear interpolation between reactant and product free energy, while the second term is an additional free-energy barrier. This barrier is given in terms of $\Delta G^{\ddagger}(0)$, which is the same intrinsic parameter used by Marcus and RW, multiplied by a n-dependent term which Agmon and Levine[6] assume to be of the form

$$M(n) = -(1-n)\ln(1-n) - n\ln n \qquad (7)$$

The correlation predicted by this treatment (eq 8) can be straightforwardly obtained by substitution of eq 7 into eq 6 followed by maximization:

$$\Delta G^{\ddagger} = \Delta G + \frac{\Delta G^{\ddagger}(0)}{\ln 2}\ln\left\{1 + \exp\left[-\frac{\Delta G \ln 2}{\Delta G^{\ddagger}(0)}\right]\right\} \qquad (8)$$

It is clear by inspection that eq 8 has the same general features (i to iii) as the RW equation. The quantitative agreement between the two functions can be checked in the sample calculation shown in Figure 1. Thus, *eq 8 and 5 are equivalent on practical grounds; owing to its more general character, the former should be preferred.* The treatment of ET reactions by eq 2 and 8, although subjected to the obvious limitations of any classical model, satisfactorily accounts for all the available kinetic data. The general expressions derived from recent nonadiabatic quantum-mechanical models[22,23,25,26] can hardly be applied to any practical case. Sample calculations, however, indicate that the predictions of such quantum models tend to approach those of the simple classical model based on eq 2 and 8.

As shown by Figure 1, the Marcus quadratic equation (eq 3) is a good approximation to eq 8 in the range $|\Delta G| \leq 4\Delta G^{\ddagger}(0)$. The "linear" free-energy relationships (eq 4) can be viewed as tangents to the eq 8 curve.[45] The slopes of such "linear" plots have to be in the range $0 < \alpha < 1$, with values lower or higher than 0.5 for exo- or endoergonic reactions, respectively.[46] For values different from 0 and 1, "linear" relationships can only be valid for more or less narrow ranges of ΔG, depending on the curvature of the eq 8 plot, i.e., on the $\Delta G^{\ddagger}(0)$ value.

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Kinetics of the Thermal Decomposition of a 1,1-Dialkyldiazene, *N*-(2,2,6,6-Tetramethylpiperidyl)nitrene

Sir:

The rates and activation parameters of 1,1-diazene thermal reactions are not known.[1] Recent theoretical studies suggest that the C–N bond strength of the 1,1-dialkyldiazene is substantially lower than that of the trans-1,2 isomer.[2] The homolytic decomposition of *N*-(dimethylamino)nitrene (**1**) is calculated to be endothermic by 23.5[2a] and 26.2,[2b] kcal/mol, respectively.

1

We report the kinetics of the thermal decomposition of a 1,1-dialkyldiazene. The temperature dependence of the unimolecular rate (k_1) of *N*-(2,2,6,6-tetramethylpiperidyl)nitrene (**2**) fragmentation was examined in three different solvents, and kinetic evidence for a direct bimolecular pathway (k_2) for the formation of tetrazene **3** from 1,1-diazene **2** is provided (Scheme I).

We recently described the direct spectroscopic observation (−78 °C) of a 1,1-dialkyldiazene, *N*-(2,2,6,6-tetramethylpiperidyl)nitrene (**2**).[3] Treatment of 1-amino-2,2,6,6-tetramethylpiperidine (**4**) with *tert*-butyl hypochlorite and triethylamine in dimethyl ether at −78 °C affords, in addition to an insoluble white precipitate (Et_3NHCl), an intense purple solution of **2** that is kinetically persistent at −78 °C but decolorizes rapidly at 0 °C. The visible (λ_{max} (CH_2Cl_2) 541 nm) and infrared (ν(N=N) 1595 cm^{-1}) spectra of **2** provided ex-

Scheme I