J. Am. Chem. Soc. 1981, 103, 2519-2523

is too low to be directly involved in the photochemical reaction. It is impossible from either of these experimental results to say whether the transient species is produced after the absorption of the first or the second photon in the two-photon photochemical process.

Although the absorption and photochemical action spectrum are similar they cannot, by suitable normalization, be superimposed as would be the case if $b_{11,2}$ in eq 5 were 0. This allows us to conclude that the second-step photochemical-action spectrum includes the region from 600 to 560 nm. Using lines from the Ar$^+$ laser, we have shown that the second-step absorption extends at least to 488 nm. Whatever the nature of the photochemical intermediate, its absorption spectrum in the 488–600-nm region is similar to but not identical with the DMST $S_0 \rightarrow S_1$ absorption.

Conclusions

In this paper we have used a new holographic technique to provide information about the two-photon photodissociation of DMST in PVK. The very fact that holograms can be produced in this system with modest CW laser powers means that the intermediate produced in the photochemical process cannot have a lifetime on the nanosecond or shorter time scales. This rules out vibrationally unrelaxed excited states and the lowest singlet state. The lowest triplet state also seems an unlikely candidate.[3a] This means that the intermediate is most likely a distinct metastable chemical species.

We have also investigated the photochemical action spectrum of this intermediate. The action spectrum is similar to but not identical with the $S_0 \rightarrow S_1$ DMST absorption. The action spectrum does not extend to the long-wavelength side beyond 600 nm. This clearly rules out the possibility that the previously observed transient with absorption in the 600–700-nm region[7,8] is involved directly in the second step of the photochemistry.

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Free-Energy Relationships for Reversible and Irreversible Electron-Transfer Processes

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Abstract: The relationship between the free-energy change and the activation energy for electron-transfer reactions is examined. Two general classes of processes, reversible and irreversible, are discussed, and the relation between them is studied. An analysis of the differences between linear and nonlinear free-energy relationships is presented.

I. Introduction

It is frequently observed that for a set of related chemical reactions there is a relationship between the free energy of activation, $\Delta G^{\ddagger}$, and the standard free-energy change, ΔG. The formulation and meaning of such free-energy relationships (FER) have been widely discussed in the past, particularly as they pertain to proton[2]- and electron[3]-transfer processes where extensive kinetic data are available. The introduction of electronically excited molecules as reactants in electron-transfer processes has generated new sets of data, and this has caused renewed interest in the experimental and theoretical aspects of FER.

Electron-transfer processes have been studied in our laboratories using different substrates (organic peroxides[4] and transition metal complexes[5]) and pursuing different aims (elucidation of the mechanism of bioluminescent and chemiluminescent displays[4] and the design of systems for the conversion of light into chemical energy[5]). In several cases these studies have led us to observe correlations between kinetic and thermodynamic quantities and to use these correlations as a means for obtaining deeper insight into these reaction mechanisms. In two independent papers[6,7] we recently discussed some general aspects of electron-transfer kinetics and apparently arrived at contradictory conclusions about the validity and the meaning of *linear* FER. The purpose of this paper is to analyze and to compare our different approaches in order to clarify their scope and limitations with the aim of removing the apparent contradiction.

II. Kinetic Scheme

An electron-transfer reaction originating from a weak interaction[8] between a donor and an acceptor can be discussed on the basis of the scheme in eq 1, where the electronic states of D and

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[2] (a) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891. (b) Kresge, A. J. *Chem. Soc. Rev.* **1973**, *2*, 245. (c) Bell, R. P. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 2088, and references cited therein. (d) Murdoch, J. R. *J. Am. Chem. Soc.* **1980**, *102*, 71 and references cited therein. (e) Albery, N. J. *Annu. Rev. Phys. Chem.* **1980**, 227.

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[4] Schuster, G. B. *Acc. Chem. Res.* **1979**, *12*, 366 and references cited therein.

[5] (a) Ballardini, R.; Varani, G.; Indelli, M. T.; Scandola, F.; Balzani, V. *J. Am. Chem. Soc.* **1978**, *100*, 7219. (b) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1. (c) Indelli, M. T.; Scandola, F. *J. Am. Chem. Soc.* **1978**, *100*, 7732. (d) Balzani, V.; Bolletta, F.; Scandola, F.; Ballardini, R. *Pure Appl. Chem.* **1979**, *51*, 299.

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[7] Scandola, F.; Balzani, V. *J. Am. Chem. Soc.* **1979**, *101*, 6140; *Ibid.* **1980**, *102*, 3663.

[8] Classical cases of weak-interaction electron-transfer processes are outer-sphere electron-transfer reactions of transition metal complexes in polar solvents.[3]

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$$\mathrm{D} + \mathrm{A} \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} \mathrm{D}...\mathrm{A} \underset{k_{32}}{\overset{k_{23}}{\rightleftarrows}} \mathrm{D}^{+}\cdot ...\mathrm{A}^{-}\cdot \xrightarrow{k_{30}} \mathrm{P} \qquad (1)$$

A are left unspecified, k_{12} and k_{21} are the diffusion and dissociation rate constants of the encounter complex,[9] k_{23} and k_{32} are the rate constants for forward and back electron transfer in the encounter, and k_{30} comprises all the possible processes (except that leading back to D...A) by which the $D^{+}\cdot ...A^{-}\cdot$ ion pair[9] can be consumed. Some of the possible processes represented by k_{30} may be thermodynamically reversible (e.g., the diffusion apart of $D^{+}\cdot$ and $A^{-}\cdot$), whereas others may be irreversible (e.g., the dissociation of $A^{-}\cdot$ into fragments). In the early stages of the overall process described by k_{30} the electron transfer can be considered kinetically irreversible because the extent of the opposing reactions is negligible even for thermodynamically reversible reactions. Application of the usual steady-state approximations to the concentrations of D...A and $D^{+}\cdot ...A^{-}\cdot$ leads to the following equation for the experimental rate constant of formation of P:[10]

$$k_p = \frac{k_{12}}{1 + \dfrac{k_{21}}{k_{23}} + \dfrac{k_{32}}{k_{23}}\dfrac{k_{21}}{k_{30}}} \qquad (2)$$

The key step of eq 1 is the electron transfer in the encounter complex. Using a classical approach,[11] k_{23} and the ratio k_{32}/k_{23} are given by

$$k_{23} = k^{\circ}_{23}e^{-\Delta G^{\ddagger}_{23}/RT} \qquad (3)$$

$$k_{32}/k_{23} = e^{\Delta G_{23}/RT} \qquad (4)$$

where k°_{23}, $\Delta G^{\ddagger}_{23}$, and ΔG_{23} are the frequency factor, the standard free activation energy, and the standard free-energy change of the electron-transfer step. Using eq 3 and 4, eq 2 can be transformed into eq 5:

$$k_p = \frac{k_{12}}{1 + \dfrac{k_{21}}{k^{\circ}_{23}}e^{\Delta G^{\ddagger}/RT} + \dfrac{k_{21}}{k_{30}}e^{\Delta G/RT}} \qquad (5)$$

For the reactions of some acceptor with a series of related donors (or vice versa), k_{12}, k_{21}, k°_{23}, and k_{30} can be considered constant; thus k_p is expected to depend only on ΔG_{23} and $\Delta G^{\ddagger}_{23}$. In turn $\Delta G^{\ddagger}_{23}$ can be expressed as a function of ΔG_{23} (FER), and, therefore, k_p can be formulated as a function of only ΔG_{23}.

Prior to further discussion of eq 5, it is important to clarify the meaning of ΔG_{23}. When the products of the electron-transfer step (i.e., $D^{+}\cdot$ and $A^{-}\cdot$) are thermodynamically defined species[13] and the interaction in the encounter complex is weak, the free-energy change in the electron-transfer step is related to the standard free-energy change ΔG (eq 6) for the overall net electron-transfer reaction (eq 7)

$$\Delta G = E^{\circ}(\mathrm{D}^{+}/\mathrm{D}) - E^{\circ}(\mathrm{A}/\mathrm{A}^{-}) \qquad (6)$$

$$\mathrm{D} + \mathrm{A} \rightleftarrows \mathrm{D}^{+}\cdot + \mathrm{A}^{-}\cdot \qquad (7)$$

by the following equation:

$$\Delta G_{23} = \Delta G + W_p - W_r \qquad (8)$$

where W_r is the work required to bring the reactants together and W_p is the corresponding term for the products. For weak interactions the work terms are due only to Coulombic attractions and, therefore, are practically zero when at least one of the two reaction partners is uncharged. More generally, W_r and W_p can be calculated, but usually they are very small and negligible, especially in polar solvents. Thus, the standard free-energy change of the electron-transfer step can simply be taken as equal to the standard free-energy change of reaction 6 which is given by the difference in the standard potential of the two redox couples. Such potentials are usually obtained from polarographic or cyclic voltammetric experiments. In some cases, however, the standard redox potentials of the species involved are not obtainable either because the species is not thermodynamically defined[13] or for some other experimental reason. In such cases the free-energy change of the electron-transfer step is unknown, but eq 5 can nevertheless be very useful as we will show below.

III. Thermodynamically Reversible Electron-Transfer Step

When the electron-transfer step is thermodynamically reversible ΔG_{23} can be measured, at least in principle, and $\Delta G^{\ddagger}_{23}$ can thus be expressed as a function of ΔG_{23} by means of a FER. The following are some of the FER that have been proposed and used in this regard:

(1) the Polanyi linear equation[14]

$$\Delta G^{\ddagger}_{23} = \alpha\Delta G_{23} + \beta \qquad (9)$$

(2) the Marcus quadratic equation[3a]

$$\Delta G^{\ddagger} = \Delta G^{\ddagger}(0)[1 + (\Delta G_{23}/4\Delta G^{\ddagger}(0))]^2 \qquad (10)$$

(3) the Rehm–Weller equation[15]

$$\Delta G^{\ddagger} = \frac{\Delta G_{23}}{2} + \left\{\left(\frac{\Delta G_{23}}{2}\right)^2 + [\Delta G^{\ddagger}(0)]^2\right\}^{1/2} \qquad (11)$$

(4) the hyperbolic equation derived first by Marcus[2a] for atom-transfer reactions and formulated later empirically by Agmon and Levine.[16]

$$\Delta G^{\ddagger} = \Delta G_{23} + \frac{\Delta G^{\ddagger}(0)}{\ln 2}\ln\left\{1 + \exp\left[-\frac{\Delta G_{23}\ln 2}{\Delta G^{\ddagger}(0)}\right]\right\} \qquad (12)$$

In eq 10, 11, and 12 $\Delta G^{\ddagger}(0)$ has the meaning of an "intrinsic barrier",[17] being the free energy of activation for a reaction with $\Delta G_{23} = 0$. In eq 9, α (usually $0 \leq \alpha \leq 1$) and β are empirical parameters; at $\Delta G_{23} = 0$ β is conceptually similar to, but not always equal to, $\Delta G^{\ddagger}(0)$.

Equations 11 and 12 exhibit similar behavior for the entire range of ΔG_{23} values probed.[7] For both of these equations, $\Delta G^{\ddagger}$ tends asymptotically toward zero for highly exergonic reactions, and toward ΔG_{23} for highly endergonic reactions. Such behavior seems to be intuitively reasonable. Also, eq 11 and 12, when used in eq 5, satisfactorily account for the available kinetic data for reversible systems over the entire ΔG_{23} range explored.[7]

The linear FER (eq 9) must break down for very large positive or negative ΔG_{23} values. That eq 9 has severe limitations for quantitative correlations between thermodynamic and kinetic quantities over a sufficiently broad range of ΔG_{23} is well-known.[2c] It has also been shown[7] that such linear FER can be viewed as tangents of the curves from eq 11 or 12, and thus they can be considered to be approximations of the nonlinear FER, valid over a more or less narrow ΔG range (see below).

The Marcus quadratic equation (eq 10) behaves very similarly to eq 12 for $|\Delta G_{23}| \leq \Delta G^{\ddagger}(0)$, and thus it also accounts for the experimental results concerning this ΔG_{23} range. A peculiar and famous feature of this equation is the prediction of an increase of $\Delta G^{\ddagger}$ when ΔG_{23} becomes lower than $-4\Delta G^{\ddagger}(0)$. When used in eq 5 the Marcus quadratic equation would thus predict a dramatic decrease in log k_p with increasing exergonicity (Marcus

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(9) Sometimes D...A and $D^{+}...A^{-}$ are called precursor and successor complex, respectively.[3b]

(10) For cases where either D or A is an excited state, simple quenching to the ground state without formation of radical ions may also occur. Weller, A.; Zachariasse, K. *Chem. Phys. Lett.* **1971**, *10*, 590.

(11) Quantum-mechanical treatments have also been discussed in the literature.[12]

(12) (a) Efrima, S.; Bixon, M. *Chem. Phys. Lett.* **1974**, *25*, 34. (b) Ulstrup, J.; Jortner, J. *J. Chem. Phys.* **1975**, *63*, 4358.

(13) A thermodynamically defined species is one that exists in a defined electronic state showing a distribution of vibrational–rotational states consistent with the temperature of the medium.

(14) Evans, M. D.; Polanyi, M. *Trans. Faraday Soc.* **1936**, *32*, 1340; **1938**, *34*, 11.

(15) Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 834; *Isr. J. Chem.* **1970**, *8*, 259.

(16) Agmon, N.; Levine, R. D. *Chem. Phys. Lett.* **1977**, *52*, 197.

(17) The intrinsic barrier is related to the internal and solvent nuclear rearrangements that have to occur prior to electron transfer.[3]

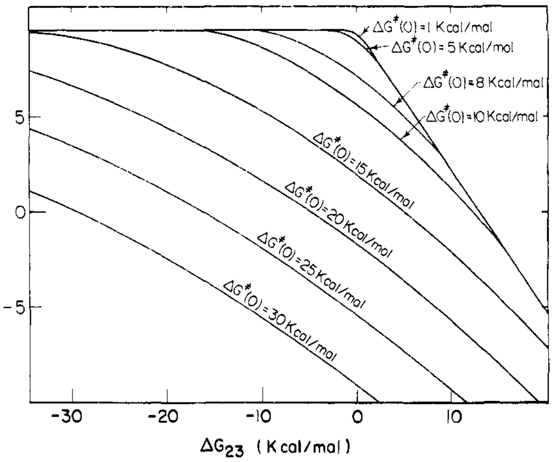

Figure 1. Response of log k_p to changes in ΔG_{23} as the value of $\Delta G^{\ddagger}(0)$ is varied.

inverted region). Until a few years ago definite proof for or against the Marcus inverted region was not available because only a few exergonic reactions had been studied. In the last few years, however, the use of electronically excited states in electron-transfer reactions (especially transition metal complexes) and the use of flash photolysis as a fast relaxation technique have permitted the exploration in a systematic way of the ΔG_{23} range corresponding to the Marcus inverted region.[5,15,18-22] No clear evidence of the inverted region has been found in fluid solution.[23] Only recently has evidence of the predicted strong decrease in the rate constant been observed for electron tunneling in rigid medium,[24a] and for electron transfer to an acceptor trapped in a cationic micelle.[24b] In conclusion, from a purely empirical point of view, when the application of a FER is over a range where $|\Delta G_{23}| >> \Delta G^{\ddagger}(0)$, the use of eq 12 (or 11) is preferable to that of eq 9 and 10.

Let us now consider the problem in more detail. When eq 12 is substituted into eq 5, the result predicts that a plot of log k_p vs. ΔG_{23} for a homogeneous series of electron-transfer reactions should consist of (Figure 1): (i) a plateau region for sufficiently exergonic reactions, (ii) an Arrhenius-type linear region (slope $1/2.3RT$) for sufficiently endergonic reactions, and (iii) an intermediate region (centered at $\Delta G_{23} = 0$) in which log k_p increases in a complex but monotonic way as ΔG_{23} decreases. Simple mathematical considerations show that the plateau value (i.e., k_p for $\Delta G_{23} \rightarrow -\infty$) is equal to

$$k_p = k_{12}k^{\circ}_{23}/(k^{\circ}_{23} + k_{21}) \qquad (13)$$

and thus it does not depend on $\Delta G^{\ddagger}(0)$.[25] On the other hand, for large and positive values of ΔG_{23} (point ii above), k_p is given by

$$k_p = \frac{k_{12}k^{\circ}_{23}k_{30}}{k_{21}(k_{30} + k^{\circ}_{23})}\, e^{-\Delta G_{23}/RT} \qquad (14)$$

and thus in this case also there is no dependence of the slope on $\Delta G^{\ddagger}(0)$. By constrast, $\Delta G^{\ddagger}(0)$ strongly affects the values of the slope in the intermediate nonlinear region. As is shown in Figure 1, for very small values of $\Delta G^{\ddagger}(0)$ the intermediate region is almost unnoticeable and the connection between the plateau and the Arrhenius straight line takes place (mediated by diffusion) in a very narrow ΔG_{23} range. As $\Delta G^{\ddagger}(0)$ increases, the nonlinear region broadens more and more, and, for this very reason, the variation of log k_p over broader and broader ΔG ranges can be approximated by straight lines, i.e., by tangents to the curve obtained by eq 5 and 12. For example, when $\Delta G^{\ddagger}(0) = 20$–$30$ kcal/mol the curve can be approximated by a tangent for about 10 units of log k_p values (Figure 1). It can be shown that the slope of the tangent is given by

$$\gamma = \frac{1}{2.3RT[1 + \exp(-\ln 2\ \Delta G_{23}/\Delta G^{\ddagger}(0))]} \qquad (15)$$

and thus must be in the range $0 \geq \gamma \geq -(1/2.3RT)$ with $\gamma = -0.5/2.3RT$ at $\Delta G_{23} = 0$, $\gamma < -0.5/2.3RT$ for positive ΔG_{23} and $\gamma > -0.5/2.3RT$ for negative ΔG_{23}. These tangents are exactly the straight lines that can be obtained from eq 5 using the linear FER of eq 9. Thus the experimental values of the slope (α) and the intercept (β) can be related to ΔG_{23} and $\Delta G^{\ddagger}(0)$ by[27]

$$\alpha = \frac{1}{[1 + \exp(-\ln 2\ \Delta G_{23}/\Delta G^{\ddagger}(0))]} \qquad (16)$$

$$\beta = \Delta G_{23}/[1 + \exp(\ln 2\ \Delta G_{23}/\Delta G^{\ddagger}(0))] + \frac{\Delta G^{\ddagger}(0)}{\ln 2} \ln\,[1 + \exp(-\ln 2\ \Delta G_{23}/\Delta G^{\ddagger}(0))] \qquad (17)$$

Note that

$$\alpha = -2.3RT\gamma \qquad (18)$$

and β is equal to $\Delta G^{\ddagger}(0)$ only for the tangent at $\Delta G_{23} = 0$, being lower than $\Delta G^{\ddagger}(0)$ for all the other tangents.

When $\Delta G^{\ddagger}(0)$ is very large (a necessary condition for "linear" behavior over a large ΔG_{23} range of the curve corresponding to eq 5 and 9), sufficiently high k_p values to be experimentally measurable can only be obtained in the exergonic region, where α is expected to be lower than 0.5 (i.e., $\gamma < -0.5/2.3RT$). Another point should be emphasized. The slope of log k_p vs. ΔG_{23} (or ΔG_{23} related quantities) has often been taken as an indication of the degree of charge transferred at the reaction transition state. It is important to note, however, that *α values between 0 and 1 are easily understood by the above model, which is based on reversible complete electron transfer.*

A number of electron-transfer reactions have been found to obey eq 5 and 12 (or 11),[5,15,18-22,26,28,29] and by best fitting procedures it is possible to evaluate important parameters like k°_{23} and $\Delta G^{\ddagger}(0)$.[30] For all such systems $\Delta G^{\ddagger}(0)$ has been determined to be small or, at least, not too large. For systems having large $\Delta G^{\ddagger}(0)$ (i.e., necessitating a large nuclear rearrangement prior to electron transfer), the standard redox potentials are usually not available because such systems behave irreversibly in dynamic electrochemical experiments. However, for a series of reactions between a homogeneous family of donors having known standard oxidation potentials and the same acceptor having an unknown, but thermodynamically defined, reduction potential, a plot of log k_p vs. $E^{\circ}(D/D^+)$ can be drawn which exhibits all the features shown before for the log k_p vs. ΔG_{23} plot. In these cases the

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(18) Ballardini, R.; Varani, G.; Scandola, F.; Balzani, V. *J. Am. Chem. Soc.* **1976**, *98*, 7432.

(19) Vogelman, E.; Schreiner, S.; Rauscher, W.; Kramer, H. E. *Z. Phys. Chem. (Frankfurt am Main)* **1976**, *101*, 321. Breyman, V.; Dreeskamp, H.; Koch, E.; Zander, M. *Chem. Phys. Lett.* **1978**, *59*, 68.

(20) Sutin, N.; Creutz, C. *J. Am. Chem. Soc.* **1977**, *99*, 241.

(21) Nagle, J. K.; Dressick, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1979**, *101* 3993.

(22) Indelli, M. T.; Ballardini, R.; Scandola, F., submitted for publication.

(23) At most "vestiges" (see ref 20) of this region have been found.

(24) (a) Beitz, J. W.; Miller, J. R. *J. Chem. Phys.* **1979**, *71*, 4579. (b) Frank, A. J.; Grätzel, M.; Henglein, A.; Janta, E. *Ber. Bunsenges. Phys. Chem.* **1976**, *80*, 294. Ulstrup, J. In "Lecture Notes in Chemistry. Vol. 10. Charge Transfer Processes in Condensed Media"; Springer Verlag: New York, 1979; pp 162–163.

(25) For $k^{\circ}_{23} << k_{21}$, $k_p = (k_{12}/k_{21})k^{\circ}_{23}$, which allows the evaluation of the imporant quantity k°_{23}.[26]

(26) Balzani, V.; Scandola, F.; Orlandi, G.; Sabbatini, N.; Indelli, M. T. *J. Am. Chem. Soc.*, submitted for publication.

(27) The same equation has been developed by Marcus[2a] and by Agmon and Levine.[16]

(28) Martens, F. M.; Verhoeven, J. W.; Gase, R. A.; Pandit, M. K.; De Boer, T. J. *Tetrahedron*, **1978**, *34*, 443.

(29) Kikuchi, K.; Tamura, S.-I.; Iwenege, C.; Kokubun; Usui, Y. *Z. Phys. Chem. (Frankfurt am Main)* **1977**, *106*, 17.

(30) This treatment has also been successfully extended to exchange energy-transfer processes in fluid solution.[31]

(31) (a) Balzani, V.; Bolletta, F. *J. Am. Chem. Soc.* **1978**, *100*, 7404. (b) Balzani, V.; Bolletta, F.; Scandola, F. *Ibid.* **1980**, *102* 2152.

(32) Obviously the same can be done for systems constituted by a series of acceptors of know $E^{\circ}(A/A^-)$ and a donor of unknown (but defined) $E^{\circ}(D/D^+)$.

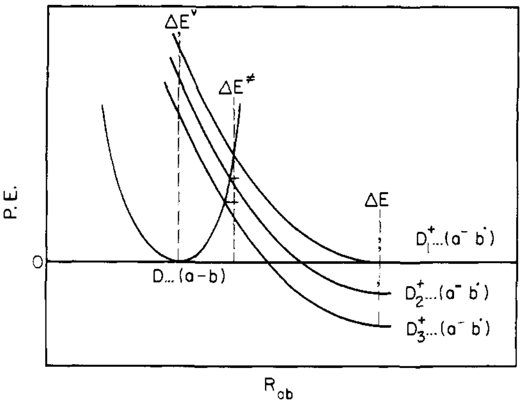

Figure 2. Plot of total energy against R_{ab} for a dissociative electron transfer from a homogeneous series of regular donors to an acceptor (a−b).

analysis of the curve may permit the determination of the $E°(D/D^+)$ value for which $\Delta G_{23} = 0$, i.e., the $E°(A/A^-)$ values.[32]

IV. Thermodynamically Irreversible Electron-Transfer Step

In some systems the electron-transfer step is part of an overall irreversible transformation. This happens, for example, when $D^{+}\cdot$ and/or $A^{-}\cdot$ undergo a very fast chemical reaction such as dissociation into two fragments. Typical cases are the cleavage of the oxygen–oxygen bond upon reduction of peroxides.[4] For such systems the situation may be schematized as shown in eq 19, where

$$D + (a\text{–}b) \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} D...(a\text{–}b) \underset{k'_{32}}{\overset{k'_{23}}{\rightleftharpoons}} D^{+}\cdot...\ (a\text{–}b)^{-}\cdot \underset{k''_{32}}{\overset{k''_{23}}{\rightleftharpoons}} D^{+}\cdot...(a^{-}\ b\cdot) \xrightarrow{k_{30}} P \quad (19)$$

(a–b) is the molecule which undergoes very rapid dissociation upon reduction and ($a^{-}b\cdot$) represents the one-electron reduction product of (a–b) after cleavage of the bond between a and b. For these molecules, electrochemical experiments give irreversible waves. The standard reduction potential corresponding to the process

$$(a\text{–}b) + e^{-} \rightarrow (a\text{–}b)^{-}\cdot \quad (20)$$

is unknown and *cannot be precisely defined if the potential energy surface of* $(a\text{–}b)^{-}\cdot$ *is dissociative along the a–b coordinate.* Thermodynamically, in these cases, what can be defined rigorously is the overall potential of the process

$$(a\text{–}b) + e^{-} \rightarrow a^{-} + b\cdot \quad (21)$$

which in principle can be measured potentiometrically or estimated from thermodynamic cycles. For these systems, an appropriate kinetic scheme is the following

$$D + (a\text{–}b) \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} D...(a\text{–}b) \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} D^{+}\cdot...(a^{-}\ b\cdot) \xrightarrow{k_{30}} P \quad (22)$$

Equation 22 is completely equivalent to eq 1.

In practice, for electron-transfer reactions between the members of a homogeneous series of "regular" donors and the same (a–b) type of acceptor (or vice versa), a linear relationship between the logarithm of the overall rate constant (or, which is equivalent, the free energy of activation) and $\Delta G'_{23}$ is often observed.[4,33] The value of $\Delta G'_{23}$ is obtained from eq 6 and 8 using the observed irreversible peak potential in the place of the standard reduction potential of the (a–b) species. The experiments give values for the slope of log k_p vs. $\Delta G'_{23}$ usually in the range from −3 to −8 V^{-1} (the slopes of the equivalent $\Delta G^{\ddagger}$ vs. $\Delta G'_{23}$ plots are thus in the range 0.2 to 0.5). This behavior can be explained in two alternative ways that will now be examined.

Linear Relationships. Consider Figure 2, where the potential energy of the system is plotted against the a–b distance. The minimum on the left-hand side corresponds to the encounter complex D...(a–b). The three dissociative curves correspond to the bond rupture of the $(a\text{–}b)^{-}\cdot$ species in the $D^{+}\cdot...(a\text{–}b)^{-}\cdot$ ion-pair obtained by electron transfer from three different donors to (a–b). Changes in solvation and other internal coordinates correspond to other dimensions of the diagram. In Figure 2 one of the donors has been taken so as to cause an overall potential energy change of zero for the process

$$D...(a\text{–}b) \rightarrow D^{+}...(a^{-}\ b\cdot) \quad (23)$$

where (a^{-} b·) represents the one-electron reduction product of (a–b) after cleavage of the bond between a and b. The figure shows the relationships among the overall potential energy change (ΔE), the vertical potential energy change (ΔE^{v}), and the potential energy change required to reach the crossing point ($\Delta E^{\ddagger}$) as the donor is changed. $\Delta E^{\ddagger}$ is a constant fraction of ΔE^{v} if we approximate the curves in the intersection region with straight lines. In the weak interaction limit changing the structure of D does not affect the potential energy of (a–b), so

$$\Delta(\Delta E) = \Delta(\Delta E^{v}) \quad (24)$$

Since for a homogeneous[5b] series of reactions the entropy change can be considered constant, we have also that

$$\Delta(\Delta G_{23}) = \Delta(\Delta E) \quad (25)$$

On the other hand, regardless of the true relationship between the irreversible reduction potential of (a–b) and ΔG_{23}

$$\Delta(\Delta G_{23}) = \Delta(\Delta G'_{23}) \quad (26)$$

In this way the uncertainty introduced by using an irreversible peak potential to define $\Delta G'_{23}$ cancels from the analysis and does not affect its validity. If we assume that the main contribution to the free activation energy comes from distortion along the a–b coordinate[34]

$$\Delta(\Delta E^{\ddagger}) = \Delta(\Delta G^{\ddagger}) \quad (27)$$

Since $\Delta E^{\ddagger}$ is a constant fraction of ΔE^{v} (see above), from eq 24 and 27 it follows that

$$\Delta(\Delta G^{\ddagger}) = \alpha\Delta(\Delta G_{23}) \quad (28)$$

and

$$\Delta(\Delta G^{\ddagger}) = \alpha\Delta(\Delta G'_{23}) \quad (29)$$

By integration

$$\Delta G^{\ddagger} = \alpha\Delta G_{23} + \beta \quad (30)$$

$$\Delta G^{\ddagger} = \alpha\Delta G'_{23} + \beta' \quad (31)$$

or in terms of k_p

$$\log k_p = -\gamma\Delta G_{23} + \beta \quad (32)$$

$$\log k_p = -\gamma\Delta G'_{23} + \beta' \quad (33)$$

In the above equations

$$\beta = \Delta G^{\ddagger}(0) \quad (34)$$

and the difference between β and β' increases with increasing degree of the irreversibility of the reduction of (a–b). Specifically, in the assumption

$$\Delta G'_{23} = \Delta G_{23} + \Delta E^{v}_{0} \quad (35)$$

it follows that

$$\beta' = \beta - \alpha\Delta E^{v}_{0} \quad (36)$$

where ΔE^{v}_{0} is the vertical potential energy change in Figure 2 for $\Delta E = 0$.

Equation 31 is more convenient to apply than eq 30 because $\Delta G'_{23}$ can usually be estimated from the redox behavior of the

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(33) (a) Thomas, M. J.; Foote, C. S. *Photochem. Photobiol.* **1978**, *27*, 683. (b) Chan, T. W.; Bruice, T. C. *J. Am. Chem. Soc.*, **1977**, *99*, 7287. (c) Bank, S.; Juckett, D. A. *Ibid.* **1975**, *97*, 567. (d) Garner, H. C.; Kochi, J. K. *Ibid.* **1975**, *97*, 1855.

(34) Strictly speaking, $\Delta G^{\ddagger} = \Delta E^{\ddagger} + c$, where c contains some ΔG-dependent terms which come from rearrangements along other coordinates of the system. Since changes in $\Delta G^{\ddagger}$ involve changes in ΔG, and c terms in eq 27 do not cancel exactly.

species involved whereas ΔG_{23} is rarely known. Note that in eq 31 $\Delta G^{\ddagger}$ will normally be smaller than $\Delta G'_{23}$ because β' is very small and α is between zero and one. This commonly observed, but recently interpreted by Walling[35] as impossible, result (the free activation energy cannot be smaller than the free energy change of the reaction) rests on the fact that $\Delta G'_{23}$ is *not* the true free-energy change of the process, which is, in fact, ΔG_{23}. In eq 30, on the other hand, β is much greater than β' of eq 31 (see eq 36), and thus $\Delta G^{\ddagger}$ may be higher than ΔG_{23} over a broad ΔG_{23} range when ΔE^{v}_{0} is very large.

Finally, it should again be emphasized that the value of α is not related to the fraction of charge transferred in the electron-transfer step, which is taken to be unity in all cases. It should also be noted, however, that a linear free-energy relationship is not a proof of such an assumption, since a reaction via an intermediate with greater or lesser charge-transfer character (e.g., an exciplex in reactions involving excited states) is expected to show similar trends.[37] The detailed description of the electronic character of the transition state must therefore rest on other experimental evidence. For example, our examination of the reaction of organic peroxides with ground- and excited-state electron donors reveals formation of radical ion products within 10 ns (the resolution of the apparatus) and a linear FER correlation between donor oxidation potential and rate spanning a factor of 10^{11} in rate constant. These observations are entirely consistent with and suggest that the reaction is initiated by simple electron transfer originating from a weak interaction between a donor and an acceptor as defined by Marcus.[8] Moreover, they severely reduce the likelihood of formation of a covalently bonded intermediate preceding the electron-transfer step. Of course, as is correctly pointed out by Walling,[35] the precise structure of the transition is unknowable.

General Treatment. The kinetic scheme shown in eq 22 can be combined with the treatment given in section III if the irreversible process is viewed as a limiting, strongly distorted case of reversible process. Equations 2 and 12 are used,[38] where the contribution of the (a–b) species to the overall free-energy change is obtained from the free-energy change of eq 21. If, as is usually the case, this last quantity is unknown, it is kept as an unknown parameter. A plot of log k_p vs. $E°(D/D^+)$ will exhibit the same features as the previously discussed plot of log k_p vs. ΔG_{23} shown in Figure 1. The only difference is that the zero of the free-energy scale in the abscissa is not known. Since the electron transfer from D...(a–b) to D^+...(a^- b·) involves extensive nuclear rearrangements (mainly related to the cleavage of the a–b bond (Figure 2)), it is to be expected that $\Delta G^{\ddagger}(0)$ can be very large so that in the log k_p vs. $E°(D/D^+)$ plot the intermediate region (see point iii of the previous discussion concerning Figure 1) will be very broad. If $\Delta G^{\ddagger}(0)$ is of the order of 20–30 kcal/mol, a very flat log k_p vs. $E°(D/D^+)$ curve, which can practically be exchanged for its tangents over large $\Delta E°(D/D^+)$ ranges, is obtained (Figure 1). As shown in section III, the tangent at $\Delta G_{23} = 0$ has slope $\gamma = -0.5/2.3RT$ (i.e., $\alpha = 0.5$ for the $\Delta G^{\ddagger}$ plot), whereas those for positive or negative ΔG_{23} have γ lower or higher than $-0.5/2.3RT$. Since the reaction implies a large $\Delta G^{\ddagger}(0)$, measurable values for k_p will usually be obtained only for negative ΔG_{23} values, so that the slope will usually be less than $-0.5/2.3RT$. As previously mentioned, each tangent is equivalent to a linear free-energy relationship of the kind in eq 32, whose analogy with the other kind of linear FER given by eq 33 had already been discussed.

V. Conclusion

A treatment for a homogeneous series of reversible and irreversible electron-transfer reactions has been given in terms of linear and nonlinear FER. It has been shown that linear FER are particular cases of more general nonlinear ones. In the nonasymptotic regions linearity can be observed over extended ΔG ranges when the nuclear rearrangements that have to occur prior to electron transfer in order to obey the Franck–Condon principle are very large. This is usually (but not only) the case of electron-transfer processes involving an irreversible step like bond cleavage upon electron transfer. The values of the slopes and intercepts of the linear plots are related to such nuclear rearrangements and not to the extent of charge transferred. This last quantity is to be determined from other experimental or theoretical arguments.

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[35] Walling, C. *J. Am. Chem. Soc.* **1980**, *102*, 6854. Walling uses ΔG_{23}, rather than $\Delta G'_{23}$ (as defined above and in our original communication[36]) or ΔG_{23} and the appropriate estimate of the magnitude for $\Delta G^{\ddagger}(0)$ (see general treatment below) to generate his comparison of the reaction free energy and the free energy of activation that leads to his generation of an "obvious impossibility". This confusion leads Walling to suggest that the observation of a value of α less than unity implies the operation of some reaction mechanism other than complete electron transfer at the reaction transition state. This point is discussed fully below.

[36] Footnote 7 in ref 6.

[37] (a) Kochevar, I. E.; Wagner, P. J. *J. Am. Chem. Soc.* **1972**, *94*, 3859. (b) Gutteplan, J. B.; Cohen, S. G. *Ibid.* **1972**, *94*, 4040. (c) Monroe, B. M.; Lee, C. G.; Turro, N. J. *Mol. Photochem.* **1974**, *6*, 271. (d) Wilkinson, F.; Garner, A. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 222.

[38] It may be that for such highly distorted situations the usual FER (cf. ref 12) is not quantitatively accurate. However, the qualitative features of such FER (such as those shown in Figure 1) are likely to be still valid.