the same experimental conditions (i.e., when the photosynthetic apparatus was oversaturated with light).[14]

Figure 5 shows the results of studies of *Rps. rubrum* wild type, where the same interpretation as given above seems likely, namely, that in the untreated cells of *Rps. rubrum* wild type a carotenoid triplet lying outside the reaction center is excited owing to the closure of the reaction center trap during the light modulated experimental sampling time. This assignment is supported by the fact that the polarization pattern for this triplet is *eae aea* (i.e., not radical pair polarized). Reduction of the cells, however, leads to the observation of a completely different triplet state at the higher temperature which is polarized *eaa eea* (radical pair polarized), reflecting its ability to trap excitation from the $BChl_2$ special pair. The spectrum of the reduced cells at lower temperatures shows a convolution of two triplet states, one of which clearly belongs to the $BChl_2$, the other being residual signals from the carotenoid system.

It is interesting to note the trends in the magnitudes of the zero-field splitting parameters of the triplets assigned to the carotenoids. The carotenoid in the reaction center of *Rps. sphaeroides* wild type has a significantly larger $|D|$ value than the reaction center carotenoid from *Rps. rubrum* wild type. Thin layer chromatography[16] of pigments from *Rps. rubrum* cells grown in our laboratory revealed only one carotenoid, identified as spirilloxanthin.[27] Reaction centers of *Rps. sphaeroides* wild type contain only spheroidene.[16] The observed differences in the $|D|$ values may be understood in terms of the extent of electron delocalization within the carotenoid molecules. Spirilloxanthin contains a chain of 13 conjugated carbon–carbon double bonds, whereas spheroidene contains only 10. The lesser extent of delocalization in the spheroidene molecule could lead to increased dipolar interaction between the unpaired electrons in the triplet state of this system, and hence a larger $|D|$ value. Because cells of *Rps. rubrum* wild type contain only one carotenoid species, we might expect the $|D|$ parameter to remain the same in both the reaction center and antenna systems. This is not the case (Table I). The reaction center carotenoid $|D|$ value is significantly smaller than that of the antenna carotenoid, suggesting that environmental or conformational effects may be important in this analysis. *Rps. sphaeroides* triplets show the same trend. More studies on the triplet states of carotenoids explaining the effects of conjugation and environment on the zero-field splitting parameters must be done before further discussion can be made.

The final system to be discussed is the triplet state of β-carotene in micelles. Despite numerous attempts to view the triplet state in organic solvents by EPR, we were unable to detect the triplet state of β-carotene in these media. It is well known that the excitation of the triplet state of β-carotene via singlet–triplet intersystem crossing is not a highly favored process.[8,9] As previously mentioned most sucessful attempts to see the triplet state of β-carotene have been through the use of triplet sensitizers in solution along with the β-carotene and using flash photolysis techniques. The structure of the β-carotene molecule may be such that photochemical or vibrational (radiationless) relaxation competes even at 77 K with the singlet–triplet intersystem crossing process. Only when these modes of relaxation are made less probable can the intersystem crossing process respond favorably. Incorporation of the β-carotene in micelles or vesicles allows this to occur. Similar effects have been observed for the triplet states of various aromatic hydrocarbons.[28]

It is known that β-carotene is a component of green plant reaction center preparations.[29] Because of the similarity between the β-carotene triplet state spectrum presented here and that observed in green-plant preparations and published previously,[11] we conclude that the triplet state viewed in these preparations is likely to be that of β-carotene. This same triplet state was also observed in green-plant preparations using optical detection of magnetic resonance techniques.[30]

This new method of detecting carotenoid triplet states can now be used to probe the structure and function of carotenoids not only in photosynthetic systems but in other carotenoid-containing biological samples as well.

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A Thermodynamic Derivation of the Cross-Relations for Rates of Electron-Transfer Reactions

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Abstract: A derivation of the cross-relations first given by Marcus, which predict the rate of electron-transfer reactions from the rates of electron-exchange reactions and the standard free energy change, is given. The derivation is based solely on thermodynamic cycles and the principle of detailed balance; the usual microscopic or mechanistic assumptions are not necessary, but we do assume independent activation of the reaction partners. Thus cross-relations should hold even in many cases for which other predictions of any given electron-transfer theory may fail. Comments are made on the possible causes for breakdown of the cross-relations; in particular, a correction factor akin to the one introduced by Marcus becomes apposite when the overall exoergicity is large, and under these conditions independent activation is no longer a valid assumption.

Introduction

Measurements of electron-transfer (ET) rates are usually discussed in terms of the theoretical framework developed by Marcus.[1–4] In particular, the Marcus cross-relations between the rates of electron exchange (EE) and ET reactions are often em-

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(1) For a convenient general review, cf. W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer", Ronald Press, New York, 1966.

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ployed to deduce rates for reactions which are difficult to measure directly.[5] The cross-relations were first derived by Marcus in the context of his activated-complex theory of ET reactions, based on his derived expression for homogeneous ET rates. Their validity has been established experimentally for a large number of systems,[4-6] and they have proven a valuable tool in determination of ET rates.[7] We wish in this paper to point out that the cross-relations may be derived on rather general thermodynamic grounds, and that, therefore, they should be valid even when some other aspects and assumptions of the Marcus analysis fail to hold.

The method used in this paper is the construction of a thermodynamic cycle for the free energy of activation of the ET reaction in terms of the free energies of activation of the two EE reactions. The use of cycles for the determination of free energies of activation has been proposed and discussed in ref 8. Here we discuss a novel application of this approach.

Consider the three homogeneous ET reactions

$$\mathrm{A^- + A^* \xrightarrow{k_{AA}} A + A^{*-}} \tag{1}$$

$$\mathrm{B^- + B^* \xrightarrow{k_{BB}} B + B^{*-}} \tag{2}$$

$$\mathrm{A^- + B \xrightarrow{k_{AB}} A + B^-} \tag{3}$$

where A and B are chemical species and the asterisk denotes an isotopic variant. The Marcus cross-relations are[1-4]

$$k_{AB} = (k_{AA}k_{BB}K_{AB}f)^{1/2} \tag{4}$$

where K_{aB} is the equilibrium constant of (3), and where

$$\ln f = [\ln k_{AB}]^2/4 \ln (k_{AA}k_{BB}/Z^2) \tag{5}$$

and Z is the collision frequency ($\sim 10^{11}$ M^{-1} s^{-1}) between reacting species.

II. Thermodynamic Derivation of the Cross-Relations

To derive (4), we consider the relative energies of ground-state and activated components. The transition states $A^\ddagger$ and $B^\ddagger$, which correspond to reactive reactants, are assumed to have free energies $G(A^\ddagger)$ and $G(B^\ddagger)$, independent of each other; this means that the activation processes (solvent rearrangement, bond displacements) of each reaction partner are assumed independent of the other partner. Then the free energies of activation for the exchange reactions are

$$\Delta G^\ddagger{}_{AA} = G(A^{-\ddagger}) + G(A^\ddagger) - G(A) - G(A^-) \tag{6a}$$

$$\Delta G^\ddagger{}_{BB} = G(B^{-\ddagger}) + G(B^\ddagger) - G(B) - G(B^-) \tag{6b}$$

Hence

$$\Delta G^\ddagger{}_{AA} + \Delta G^\ddagger{}_{BB} = G(B^{-\ddagger}) + G(A^{-\ddagger}) + G(A^\ddagger) + G(B^\ddagger) - G(B^-) - G(B) - G(A^-) - G(A) \tag{7}$$

For the ET reaction (3) the free energy of activation is

$$\Delta G^\ddagger{}_{AB} = G(B^\ddagger) + G(A^{-\ddagger}) - G(B) - G(A^-) \tag{8}$$

As in other[8] applications of thermodynamic cycles for free energies of activation, here too it is advantageous to invoke the detailed-balance condition: the free energies for the reactive reactants of the forward and reverse reactions must be the same.[8] Thus we must have

$$G(B^\ddagger) + G(A^{-\ddagger}) = G(B^{-\ddagger}) + G(A^\ddagger) \tag{9}$$

Substitution of (9) into (8) yields

$$\Delta G^\ddagger{}_{AB} = \tfrac{1}{2}\{G(B^{-\ddagger}) + G(A^{-\ddagger}) + G(B^\ddagger) + G(A^\ddagger) - 2G(A^-) - 2G(B)\} \tag{10}$$

$$\Delta G^\ddagger{}_{AB} = \tfrac{1}{2}\{G(B^{-\ddagger}) + G(A^{-\ddagger}) + G(B^\ddagger) + G(A^\ddagger) - G(A^-) - G(B) - G(B^-) - G(A)\} + \tfrac{1}{2}\{G(B^-) + G(A) - G(A^-) - G(B)\} \tag{11}$$

The last term is the overall standard free energy charge of the ET reaction (3):

$$\Delta G^\circ{}_{AB} = G(B^-) + G(A) - G(A^-) - G(B) \tag{12}$$

while the first bracketed term on the right-hand side of (11) is just (7). Thus the free energy of activation for the ET reaction (3), given by (11), can be written as

$$\Delta G^\ddagger{}_{AB} = \tfrac{1}{2}\{\Delta G^\ddagger{}_{AA} + \Delta G^\ddagger{}_{BB} + \Delta G^0{}_{AB}\} \tag{13}$$

Using the exact relation[8]

$$k_{ij} = Z_{ij}e^{-\Delta G^\ddagger{}_{ij}/RT} \tag{14}$$

where Z_{ij} is a collision frequency of the reactants, (13) can be written as

$$k_{AB} = (k_{AA}k_{BB}K_{AB}F)^{1/2} \tag{15}$$

where

$$F = (Z_{AB}{}^2/Z_{AA}Z_{BB}) \tag{16}$$

If we assume (as does Marcus) a single universal value for the collision frequencies Z_{ij}, F becomes sensibly unity, and then (15) becomes the Marcus cross-relations, in their usually applied form.

III. Remarks

The present derivation is completely rigorous and requires only the following assumptions:

(a) The activation process for each chemical species is assumed to be independent of its reacting partner.

(b) The activated states $A^\ddagger$, $A^{-\ddagger}$, $B^\ddagger$, and $B^{-\ddagger}$ are assumed the same for the symmetric electron exchange reactions (1) and (2) and for the asymmetric ET reaction (3).

We note the following assumptions are not made in our derivation: (u) applicability of the Franck–Condon principle; (v) validity of activated-complex theory; (w) spin multiplicity is unchanged; (x) the potential curves are parabolic; (y) the solvent may be described as a dielectric continuum; (z) the transfers are (non)adiabatic.

This clarification of which assumptions are crucial to the derivation of (15) and which are not may prove helpful in analysis of the rate behavior of ET systems. If the cross-relations in their simple form

$$k_{12} = (k_{11}k_{22}K_{12})^{1/2} \tag{17}$$

are observed to fail for a given triad of reactions, the cause of failure must be either the breakdown of (a) or (b) or the constant F of (16) assuming a value notably different from unity; none of (u–z) will cause failure of the cross-relations. In general, one would expect (a) to be less valid for small than for large ligands,

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(2) R. A. Marcus, *Discuss. Faraday Soc.*, **29**, 21–30 (1960); *J. Phys. Chem.*, **67**, 853–857 (1963); *J. Chem. Phys.*, **43**, 679–701 (1965); in "Special Topics in Electrochemistry", P. A. Rock, Ed., Elsevier, Amsterdam, 1977.

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(4) Other covenient reviews are given by N. Sutin, *Annu. Rev. Phys. Chem.*, **17**, 119–172 (1966); in "Inorganic Biochemistry", G. L. Eichorn, Ed., Elsevier, Amsterdam, 1973; *Annu. Rev. Nucl. Sci.*, **12**, 285–328 (1962); V. G. Levich, *Adv. Electrochem. Electrochem. Eng.*, **4**, 249–371 (1966); H. Taube, "Electron Transfer Reactions of Complex Ions in Solutions", Academic Press, New York, 1970.

(5) Cf., e.g., recent work by Gray and collaborators: S. Wherland and H. B. Gray, *Proc. Natl. Acad. Sci. U.S.A.* **73**, 2950–2954 (1976); R. L. Holwerda et al., *J. Am Chem. Soc.*, **100**, 5028–5033 (1978). Also D. F. Rohrbach et al., *Inorg. Chem.*, **16**, 2650–2652 (1977); B. Brunschwig and N. Sutin, *J. Am. Chem. Soc.*, **100**, 7568–7577 (1978); C. T. Lin et al., *ibid.*, **98**, 6536–6544 (1976); M. Chou, C. Creutz, and N. Sutin, *ibid.*, **99**, 5615–5623 (1977). Early work is reported by R. J. Campion, N. Purdee, and N. Sutin, *Inorg. Chem.*, **3**, 109–194 (1964).

(6) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", Wiley, New York, 1967.

(7) Other discussions are given in ref 4–6.

(8) R. D. Levine, *J. Phys. Chem.*, **83**, 159–170 (1979).

and more valid for outer-sphere than for inner-sphere transfers. The possibility of failure of (b) will probably rest on detailed mechanistic analysis in any given case. Finally, we would expect F to differ from unity most substantially when A and B are of very different charges or sizes, or when the solvent system is highly inhomogeneous (such as for membrane-bound species).

With these generalizations in mind, we might examine two of the standard cases for which the cross-relations in the forms (17) or (4) fail to hold. The first involves the reaction[6,9]

$$\mathrm{Ce^{IV} + Fe^{II} \rightarrow Ce^{III} + Fe^{III}} \qquad (18)$$

in aqueous solution. The cross-relations (4) predict its rate as 6×10^5 M^{-1} s^{-1}, whereas experimentally the rate is roughly 700 M^{-1} s^{-1}. Similarly, for the reaction of V^{III} with Cr^{III}, the observed rate is 60 times the calculated one,[6] and a large number of reactions of Co^{II}/Co^{III} are observed to show large deviations[6,10] from (4). Other well-documented cases include reactions between actinides.[11] Among the explanations suggested in the literature for these deviations are (1) changes in spin multiplicity; (2) substantial changes in the inner-sphere geometry; (3) formation of binuclear intermediates; (4) inner-sphere mechanisms for k_{12}, while outer-sphere behavior occurs for k_{11}, k_{22}; (5) atom transfer, as opposed to ET, as the actual mechanism.

Based on our simple thermodynamic arguments, both (1) and (2) may be dismissed as possible expanations: both of them are already included in the free energies of (13). If (3) occurs, our assumption (a) will break down, while if (4) holds both (a) and (b) will fail. Although a similar analysis in terms of thermodynamic cycles holds for atom-transfer reactions,[8] mixing atom transfer (for k_{12}) and ET (for k_{11} and k_{22}) will not yield (13). Generally, if the observed rate is larger than that calculated from (4), one would tend to blame (3), (4), or (5), while, if the converse is true, either (5) or (6) if $Z_{AB}{}^2$ differs considerably from $Z_{AA}Z_{BB}$ may be to blame. For (18) this might be so, since the Coulombic barrier against successful IV/III collisions should be substantially greater than that against II/III collisions.

We would like to remark on the difference between the Marcus f of (4) and F of (16). The Marcus expression derives specifically from his solvent dielectric model, in particular from his Gaussian-type form for the effective activation free energy. Our form, on the other hand, does not result from any microscopic model of the activation process. The expression (4) has the advantage of known form (given the exchange rates ΔG_{AB} and Z), but it does depend on a specific microscopic picture, which may fail (for instance, in the "abnormal", highly exoergic regime).[12] Expression (16) is more general, but, except for qualitative statements ("high charge and large bulk reduce Z"), it is difficult to make quantitative.

The Brønsted coefficient

$$\alpha = -\partial \ln (k_{AB}/z_{AB})/\partial(\Delta G_{AB}/RT) \qquad (19)$$

is precisely +1/2 for our rate relationship (15). This predicts that the rate k_{AB} will continue to increase without limit as the reaction becomes more exoergic (that is as ΔG_{AB} becomes more negative). The Marcus form (4), on the other hand, predicts that the rate will start to decrease beyond a certain critical exoergicity; this high-exoergicity realm is often referred to as the inverted region. Other forms for k_{12} predict differing behavior in this region (slower falloff[12a] or constant[13]). We simply note that α *must* be +1/2 unless either (a) or (b) fails or one of (3–6) occurs. The most probable cause is the failure of (a); this has been remarked on previously[14] and modified forms involving the parameter α have been defined. One expects on general grounds[15] that $\alpha \approx 1/2$ for $\Delta G_{AB} \approx 0$, and that for $\Delta G_{AB} \ll 0$ α will be quite small with the transition state resembling the collision complex of the reactants; thus the activation is not independent, and (15) will fail.

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(13) N. Agmon and R. D. Levine, *Chem. Phys. Lett.*, **52**, 197–200 (1977).

(14) Cf., e.g., ref 1, p 135.

(15) R. W. Lumry and H. Eyring, *J. Phys. Chem.*, **58**, 110 (1954).

Matrix Photoionization and Radiolysis of Boron Trihalides. Infrared and Ultraviolet Spectra of $BCl_3{}^+$ and $BBr_3{}^+$ and Infrared Spectra of BCl_2 and BBr_2

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Abstract: Infrared spectra of argon/boron trihalide mixtures deposited onto a cesium iodide window at 15 K with simultaneous proton radiolysis revealed boron isotopic absorptions for ν_4 and ν_5 of $HBCl_2$ and $HBBr_2$; isotopic splittings clearly show that ν_4 is the in-plane deformation and ν_5 is the antisymmetric B–X$_2$ stretching mode. Irradiation of boron trihalide samples with a windowless argon resonance lamp generated sharp infrared absorptions due to both boron isotopes of a new product on the high-energy side of the strong ν_3 parent absorptions. These bands, which disappeared on photolysis with a filtered high-pressure mercury arc, are assigned to the parent cations $BCl_3{}^+$ and $BBr_3{}^+$. Optical absorption spectra of similarly produced samples gave broad, photosensitive bands in the near-ultraviolet; these band positions agree with energy differences between bands in the photoelectron spectra. Both radiolysis and vacuum ultraviolet photolysis produced bihalide ions $HX_2{}^-$ and boron isotopic absorptions just above the precursor absorptions which are assigned to ν_3 of BCl_2 and BBr_2. Boron isotopic data provides a 125 ± 5° determination of the bond angles for these free radicals.

Introduction

The observation of small reactive halides of first-row elements has developed rapidly over the past decade through the use of matrix isolation spectroscopy. The matrix techniques discussed in this paper in addition to metal atom reactions have been used in studies of carbon,[1-7] nitrogen,[8-11] and oxygen[12-15] halides in this