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## **Remarks on Free-Energy Correlations of Rate Constants for Electron-Transfer Quenching** of Electronically Excited States

Sir:

Following the pioneering work of Weller,<sup>1</sup> the electrontransfer quenching of electronically excited states has been actively investigated in the past decade.<sup>2-8</sup> In most of the systems studied, the quenching process was not accompanied by permanent chemical changes, indicating that the primary electron-transfer process is rapidly reverted in the dark. The elementary steps involved in a reversible electron-transfer quenching mechanism are shown in Scheme I.

The kinetics associated with such a scheme has been first worked out by Rhem and Weller<sup>4,5</sup> (RW) and their treatment has been thereafter followed by most workers in this field.<sup>2,3,6-8</sup> On the basis of steady-state considerations, the experimental bimolecular quenching constant,  $k_q$ , can be expressed as

$$k_{q} = \frac{k_{12}}{1 + (k_{21}/k_{23}) + (k_{21}k_{32}/k_{30}k_{23})}$$
(1)

The rate constants of the three electron-transfer steps in Scheme I, i.e.,  $k_{23}$ ,  $k_{32}$ ,  $k_{30}$ , obey the general equation

$$k_{ij} = Z_{ij} \exp[-(\Delta G^{\ddagger}_{ij}/RT)]$$
(2)

where  $Z_{ij}$  is the frequency factor and  $\Delta G^{\pm}_{ij}$  is the activation free energy of the process. If eq 2 is substituted into eq 1 for all three electron-transfer steps, the following equation

$$k_{q} = \frac{k_{12}}{1 + \frac{k_{21}}{Z_{23} \exp\left(-\frac{\Delta G^{\ddagger}_{23}}{RT}\right)} + \frac{k_{21}}{Z_{30} \exp\left(-\frac{\Delta G^{\ddagger}_{30}}{RT}\right)} \exp\left(\frac{\Delta G_{23}}{RT}\right)}$$
(3)

is obtained, where  $\Delta G_{23}$  is the overall free-energy change associated with the forward electron-transfer process. In their classical work,<sup>4,5</sup> RW assume that  $k_{30}$  can be taken as a common frequency factor, Z, for all three electron-transfer processes because "since the free energy gained in  $\ldots k_{30} \ldots$ is exceedingly large,  $\Delta G^{\pm}_{30}$  can be assumed to be close to zero". This simplifying assumption leads to the following expression for the bimolecular quenching constant:

$$k_{q} = \frac{k_{12}}{1 + (k_{21}/Z)[\exp(\Delta G^{\ddagger}_{23}/RT) + \exp(\Delta G_{23}/RT)]}$$
(4)

ą logka -30 -20 -10 <sup>0</sup> ∆G<sub>23</sub> kcal/mole

10

Figure 1. Free-energy correlation of rate constants for electron-transfer quenching calculated<sup>10</sup> from eq 4 plus eq 6 (curve a) or eq 5 (curve b).



This expression can be used to calculate the dependence of the bimolecular quenching constant on the overall free-energy change, provided that a functional relationship between  $\Delta G^{\ddagger}_{23}$ and  $\Delta G_{23}$  is assumed. Two options are presently available in this regard. The first one is the classical relationship from the Marcus theory<sup>9</sup> of outer-sphere electron transfer reactions:

$$\Delta G^{\ddagger}_{ij} = \Delta G^{\ddagger}_{ij}(0) \{ 1 + [\Delta G_{ij}/4\Delta G^{\ddagger}_{ij}(0)] \}^2$$
(5)

The second one is an empirical relationship proposed by RW:4,5

$$\Delta G^{\ddagger}_{ij} = \{ [(\Delta G_{ij}/2)]^2 + [\Delta G^{\ddagger}_{ij}(0)]^2 \}^{1/2} + (\Delta G_{ij}/2)$$
(6)

In eq 5 and 6,  $\Delta G^{\dagger}_{ij}(0)$  is the activation free energy the reaction should have if no overall free energy change occurred, a quantity often called the "intrinsic barrier" to the electrontransfer process.

The dependence of the bimolecular quenching constant on the overall free-energy change predicted by eq 4 after substitution with eq 5 or eq 6 is shown in Figure 1. Curve b is calculated using the Marcus expression (eq 5), while curve a is calculated using the RW one (eq 6).<sup>10</sup> Both plots have an almost identical Arrhenius-type portion in the endoergonic region and a plateau in the slightly exoergonic region, but a sharp difference between the two curves shows up in the highly exoergonic region. In this region, according to RW the quenching constants remain on the plateau, whereas according to Marcus they should exhibit a sharp drop, usually called "inverted" behavior. The highly exoergonic region has only been specifically investigated in a limited number of studies.<sup>2,3,6-9</sup> However, the available experimental results clearly show that the RW relationship (eq 6) is obeyed, while no clear evidence for inverted behavior has so far been reported.<sup>11</sup>

In this communication, we would like to point out a particular feature of this kinetic system which seems to have been largely overlooked in the past. It should be realized that the ability of the Marcus (eq 5) or RW (eq 6) relationships to interpret the experimental results cannot be tested by introducing these equations into eq 4, since this equation originates from an assumption (i.e.,  $k_{30} \approx Z$ ) which already implies an anti-Marcus behavior for the back-electron-transfer step. Rather,

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Figure 2. Free-energy correlation of rate constants for electron-transfer quenching calculated<sup>10</sup> from eq 3 and 7 plus eq 6 (curve a) or eq 5 (curves b, c, d); curves b, c, and d refer to  $E_{0-0}$  values in eq 7 of 40, 55, and 70 kcal/mol, respectively.

eq 3, which is "neutral" in this regard, should be used. If this is done, it can be shown that the discrepancy between the correlations predicted using Marcus and RW functions is even more dramatic than that shown in Figure 1.

Equation 3 can be used to calculate  $k_q$  as a function of  $\Delta G_{23}$ by using either Marcus (eq 5) or RW (eq 6) functions for both  $\Delta G^{\ddagger}_{23}$  and  $\Delta G^{\ddagger}_{30}$ . This is facilitated by the assumption of equal intrinsic barriers for both-electron-transfer processes,<sup>13</sup> and by consideration of the energetics of the system given by

$$\Delta G_{30} + \Delta G_{23} = -E_{\text{o-o}} \tag{7}$$

where  $E_{o-o}$  is the spectroscopic energy of the excited state.<sup>14</sup> The results of such a calculation<sup>10</sup> are shown in Figure 2. Curve a is calculated with the RW function and is practically independent of the  $E_{o-o}$  value used. Curves b, c, and d are calculated with the Marcus function with  $E_{o-o}$  values of 40, 55, and 70 kcal/mol, respectively. As expected, curve a is almost identical with curve a of Figure 1. Curves b, c, and d, on the other hand, show the "inverted" region in the highly exoergonic part (similarly to curve b in Figure 1). However, they also show a sharp drop in the quenching constants relative to curves a in the "normal" region. The physical reason behind this behavior is that in the "normal"  $\Delta G_{23}$  region, the back electron transfer to the ground state is, according to the Marcus function, in the "inverted"  $\Delta G_{30}$  region. In these cases, back electron transfer to the excited state,  $k_{32}$ , predominates over that to the ground state,  $k_{30}$ , with the consequence of a strongly reduced quenching effect. Obviously, the departure from the wellbehaved curves a in the normal region becomes more and more dramatic as the energy of the excited state is increased (curves b, c, and d of Figure 2).

In conclusion, the use of the Marcus model for free-energy correlation of rate constants of excited-state electron-transfer quenching leads to a much more serious disagreement with experimental results than previously believed. In particular, the model predicts unobserved inefficiencies not only in the highly exoergonic "inverted" region, but also in the commonly investigated slightly exo- or endoergonic, "normal" region.

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- (10) The calculation has been performed using the following set of parameters:  $k_{12} = 1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{21} = 8.7 \times 10^9 \text{ s}^{-1}$ ,  $Z = 6.2 \times 10^{12} \text{ s}^{-1}$ ,  $\Delta G^+_{23}(0) = 3.0 \text{ kcal/mol}$ , T = 298 K. The qualitative features of Figures 1 and 2 are not affected by varying these values within reasonable ranges.
- (11) "Vestiges" of the inverted region have been recently reported for electron-transfer quenching of ruthenium(II) polypyridine complexes, <sup>12</sup> although the observed effect is orders of magnitude too small compared with the expectations of the Marcus model.
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- (14) Equation 7 holds if the entropy changes associated with the excitation are small,<sup>2.5</sup> a condition met by most of the systems studied so far.

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# 1,1-Difluoro-2,2,3,3-tetramethyl-1-silirane: Synthesis and Novel Chemistry. Reinterpretation of Difluorosilylene Reaction Mechanisms

Sir:

We reported the preparation of hexamethylsilirane (1a) in 1975 and in subsequent research have studied its chemistry in some detail.<sup>1</sup> Its thermolysis at 75 °C proceeds by reversible extrusion of dimethylsilylene.<sup>1c</sup> A concomitant, irreversible process is the insertion of Me<sub>2</sub>Si into an Si-C bond of 1a to give octamethyl-1,2-disilacyclobutane.<sup>1f</sup> The dimethylsilylene thus



generated also may be intercepted with other reactants such as silicon hydrides, methoxysilanes, other olefins, and acetylenes.<sup>1b-d</sup> The synthesis and study of other siliranes of type **1**, as well as of similar siliranes with two different substituents on the silicon atom, would be of interest, especially if they also underwent silylene extrusion on thermolysis.

The generation of difluorosilylene as currently practised requires the reaction of gaseous SiF<sub>4</sub> with elemental silicon at 1100-1200 °C at low pressures.<sup>2</sup> The availability of an SiF<sub>2</sub> precursor which would release this intermediate in solution below 100 °C would be an obviously attractive improvement. In view of the intriguing results reported by Margrave and his co-workers on the reactions on SiF<sub>2</sub> with organic and inorganic substrates,<sup>2</sup> we directed our attention to the synthesis and investigation of 1,1-difluoro-2,2,3,3-tertramethyl-1-silirane (**1b**).

The synthesis of **1b** was effected using an adaptation of our procedure for hexamethylsilirane.<sup>1a</sup> Diisopropyldifluorosilane<sup>3</sup> was brominated at 95-100 °C to give bis( $\alpha$ -bromoisopropyl)-difluorosilane (**2**), mp 33-35 °C, in 75% yield. Ring closure was effected under an atmosphere of argon by reaction of the latter with 1 molar equiv of magnesium in a THF/dimethyl

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