

**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  $\Delta G_{23}^\ddagger$  and  $\Delta G_{30}^\ddagger$ . 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

$$\Delta G_{30} + \Delta G_{23} = -E_{0-0} \quad (7)$$

where  $E_{0-0}$  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  $E_{0-0}$  value used. Curves b, c, and d are calculated with the Marcus function with  $E_{0-0}$  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 well-behaved 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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#### References and Notes

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- The calculation has been performed using the following set of parameters:  $k_{12} = 1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{21} = 8.7 \times 10^9 \text{ s}^{-1}$ ,  $Z = 6.2 \times 10^{12} \text{ s}^{-1}$ ,  $\Delta G_{23}^\ddagger(0) = 3.0 \text{ kcal/mol}$ ,  $T = 298 \text{ K}$ . The qualitative features of Figures 1 and 2 are not affected by varying these values within reasonable ranges.
- "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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- The assumption of equal intrinsic barriers for excited-state and ground-state processes is justified as long as the differences in shape, size, and solvation between the states (i.e., the Stokes shift) are small.
- 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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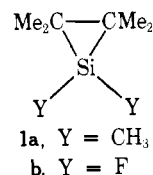
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#### 1,1-Difluoro-2,2,3,3-tetramethyl-1-silirane: Synthesis and Novel Chemistry. Reinterpretation of Difluorosilylene Reaction Mechanisms

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  $\text{Me}_2\text{Si}$  into a 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  $\text{SiF}_4$  with elemental silicon at 1100–1200 °C at low pressures.<sup>2</sup> The availability of an  $\text{SiF}_2$  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  $\text{SiF}_2$  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-tetramethyl-1-silirane (**1b**).

The synthesis of **1b** was effected using an adaptation of our procedure for hexamethylsilirane.<sup>1a</sup> Diisopropylidifluorosilane<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