## Nonvertical Deactivation and the Lifetime and Geometry of Stilbene Triplets in Solution

Sir:

A weak transient absorption at 360 nm observed in benzene solutions of *trans*-stilbene following excitation with a radiolysis pulse of 25 nsec duration has been assigned to stilbene triplets.[1] This transient's lifetime at room temperature, $\sim 110 \pm 10$ nsec,[2] is much longer than that estimated from azulene quenching experiments, ~ 10 nsec,[3-5] assuming diffusion-controlled excitation transfer from transoid triplets, ^3t, to azulene, eq 1, $k_{az} = 5 \times 10^9$ M^{-1} sec^{-1}, Scheme I. This as-

$$^3t + Az \xrightarrow{k_{az}} t + {}^3Az \qquad (1)$$
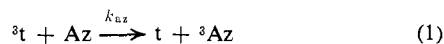
Scheme I. Old Mechanism for Stilbene Triplet Decay and Quenching
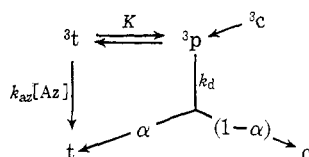
sumption is supported by (1) strong dependence of k_{az}/Kk_d ratios on solvent viscosity[6] and (2) measurement of $k_{az} = 6.7 \times 10^9$ and 6.0×10^9 M^{-1} sec^{-1}, respectively, for the quenching of indeno[2,1-a]indene[7] and 4-nitro-4'-methoxystilbene[2,8] triplets by azulene in benzene. The following experiments, prompted by the report that the quenching of nitrostilbene triplets by oxygen does not alter trans/cis photostationary ratios, $([t]/[c])_s$,[2,8] account for the lifetime discrepancy and require modification of the decay and quenching mechanisms shown in Scheme I.

Stilbene $([t]/[c])_s$ compositions were determined for the benzophenone-sensitized photoisomerization in benzene at 30° as a function of azulene concentration in the presence of air and oxygen.[9] As for degassed solutions plots of $([t]/[c])_s$ ratios *vs.* azulene are linear with the difference being a strong attenuating oxygen effect on the slopes of the lines. Slope/intercept ratios, r, and intercepts, i, are shown in Table I.

The diminished slopes of the azulene plots indicate that oxygen interacts with stilbene triplets, thereby decreasing their lifetime. The common intercept shows that the quenching event does not alter the decay ratio of the quenched stilbene triplet, suggesting that oxygen interacts with twisted triplets, ^3p, as shown in nonvertical quenching step 2. A close analogy for this

(1) F. S. Dainton, E. A. Robinson, and G. A. Salmon, *J. Phys. Chem.*, **76**, 3897 (1972).

(2) *Cf.*, also, D. V. Bent and D. Schulte-Frohlinde, *J. Phys. Chem.*, **78**, 446 (1974).

(3) J. Saltiel, J. D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton, and O. C. Zafiriou, *Org. Photochem.*, **3**, 1 (1973).

(4) J. Saltiel, J. T. D'Agostino, W. G. Herkstroeter, G. Saint-Ruf, and N. P. Buu-Hoï, *J. Amer. Chem. Soc.*, **95**, 2543 (1973).

(5) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

(6) J. Saltiel and E. D. Megarity, *J. Amer. Chem. Soc.*, **91**, 1265 (1969); **94**, 2742 (1972).

(7) J. Saltiel, A. D. Rousseau, P. T. Shannon, D. E. Townsend, and A. K. Uriarte, unpublished results.

(8) D. V. Bent and D. Schulte-Frohlinde, *J. Phys. Chem.*, **78**, 451 (1974).

(9) Air or oxygen was solvent saturated and bubbled through the irradiation ampoules. Excitation was at 366 nm, using a 450-W Hanovia lamp. Analyses were by glpc as previously described.[4] Similar observations were obtained in *tert*-butyl alcohol.

Table I. Attenuation of the Azulene Effect by Oxygen

Conditions	r	i	$10^3[O_2]$,[a] M
Degassed	120	0.69 ± 0.01	0
Air	51	0.70 ± 0.01	1.62
O_2	15	0.70 ± 0.01	7.74

[a] J. E. Jolley and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **80**, 1050 (1958).

$$^3p + {}^3O_2 \xrightarrow{k_{ox}} \alpha t + (1 - \alpha)c + {}^1O_2 \qquad (2)$$
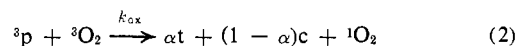
process is the quantum chain carrying step in 1,3-diene photoisomerization.[10] Since oxygen should also efficiently quench transoid triplets, ^3t, it follows that almost all stilbene triplets are twisted. Hence, the azulene effect must also have its origin in the interaction of ^3p with azulene. These ideas are incorporated in Scheme II which leads to expression 3, where k_c and k_t are rate

$$([t]/[c])_s = (k_c/k_t)\left(\frac{\alpha}{1 - \alpha}\right)\left(1 + \frac{[k'_{az}Az]}{\alpha(k_d + k_{ox}[O_2])}\right) \qquad (3)$$

Scheme II. Modified Mechanism for Stilbene Triplet Decay and Interaction with Quenchers
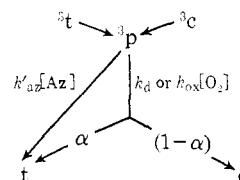
constants for excitation transfer from benzophenone triplets to *cis*- and *trans*-stilbene, respectively. The stilbene triplet lifetime can be estimated from the slope/intercept ratios in Table I, using eq 4, where r_0

$$\tau = (r_0 - r)/rk_{ox}[O_2] \qquad (4)$$

is the slope/intercept ratio for degassed solutions. Using the data in Table I and assuming $k_{ox} = 7.0 \times 10^9$ M^{-1} sec^{-1}, the value for the rate constant of nitrostilbene triplet quenching by oxygen[2] give $\tau = 119$ and 129 nsec for the air-saturated and oxygen-saturated experiments, respectively. These lifetimes are in agreement with values obtained in the pulse radiolysis experiments,[1] and since $k'_{az} = \alpha r_0/\tau$ they give $k'_{az} \simeq 4.0 \times 10^8$ M^{-1} sec^{-1}, well below the value for a diffusion-controlled process.

In contrast to azulene and other quenchers[5] which deactivate stilbene triplets to the trans isomer, quenching by di-*tert*-butyl nitroxide, N, modestly favors decay to the cis isomer, eq 5, where α' is less than α.[11]

$$^3p + N \xrightarrow{k_n} \alpha't + (1 - \alpha')c + N \qquad (5)$$
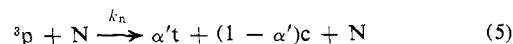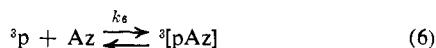
Our results suggest that the availability of an exchange quenching mechanism, not involving triplet excitation transfer,[11] allows radical N to interact with stilbene triplets in their *preferred* ^3p geometry,[12] while azulene and other triplet excitation acceptors interact with stilbene triplets only when large triplet energy

(10) J. Saltiel, D. E. Townsend, and A. Sykes, *J. Amer. Chem. Soc.*, **95**, 5968 (1973).

(11) R. A. Caldwell and R. E. Schwerzel, *J. Amer. Chem. Soc.*, **94**, 1035 (1972); **95**, 1382 (1973).

(12) Since $k_n \simeq 2.2k'_{az}$[11] revision of k'_{az} downward suggests that the efficiency of di-*tert*-butyl nitroxide quenching interactions is not very sensitive to the geometry of the quenched triplet; compare 6.3×10^8 M^{-1} sec^{-1} for naphthalene triplet quenching[11] with $k_n \simeq 9 \times 10^8$ M^{-1} sec^{-1}.

gaps are achieved in nearly planar transoid geometries. A detailed interpretation of the azulene effect would then involve eq 6–8, where brackets designate exciplexes

$$^3p + Az \xrightarrow{k_6} {}^3[pAz] \quad (6)$$

$$^3[pAz] \xrightarrow{k_7} {}^3[tAz] \quad (7)$$

$$^3[tAz] \xrightarrow{k_8} t + {}^3Az \quad (8)$$

or encounter complexes.[13] Accordingly, k'_{az} in eq 3 is replaced by the expression in eq 9, which reduces to

$$k'_{az} = \frac{k_6 K_7(k_8/k_{-6})}{(k_8 K_7/k_{-6}) + k_8/k_{-7} + 1} \quad (9)$$

eq 10 assuming that k_6, k_{-6}, and k_8 are diffusion con-

$$k'_{az} = k_{dif} K_7/(1 + K_7) \quad (10)$$

trolled and that equilibration step 7 is faster than diffusional separation of the donor–acceptor pair. This mechanism accounts for the dependence of $k'_{az}\tau$ values on solvent viscosity,[6] and, using $k_{dif} = 10^{10}\ M^{-1}\ sec^{-1}$, gives $K_7 \simeq 0.04$ in benzene at 30°.

The deactivation of stilbene triplets by oxygen to either ground state isomer suggests that the 22 kcal/mol energy gap required in eq 2, if $^1\Delta_g$ oxygen is produced, is achieved with nearly unit efficiency by torsional displacement toward either transoid or cisoid geometries. The larger energy gaps required for excitation transfer to azulene and other quenchers are apparently achieved only by torsional displacement toward transoid geometries.

Acknowledgment. This research was supported by National Science Foundation Grant GP-24265.

(13) For a related case see R. A. Caldwell, *J. Amer. Chem. Soc.*, 92, 3229 (1970).
(14) Fellow of the Alfred P. Sloan Foundation, 1971–1973.

Jack Saltiel,* [14] Babu Thomas
Department of Chemistry, Florida State University
Tallahassee, Florida 32306

Structural Evidence for Variations in the Franck–Condon Barrier to Electron Transfer between Low-Spin Cobalt(II) and Cobalt(III)[1]

Sir:

We recently reported[2] the discovery of a 0.5 Å cobalt–axial ligand distortion in low spin Co([14]dieneN₄)(OH₂)₂²⁺, and we called attention to the fact that this distortion is of sufficient magnitude to account for the very small self-exchange rate constant of the Co([14]dieneN₄)(OH₂)₂³⁺–Co([14]dieneN₄)(OH₂)₂²⁺ couple ($k_{exchange} = 2 \times 10^{-7}\ M^{-1}\ sec^{-1}$ at 70°).[3,4] In their related kinetic study, Rillema, *et al.*,[4] found the self-

(2) M. D. Glick, J. M. Kuszaj, and J. F. Endicott, *J. Amer. Chem. Soc.*, 95, 5097 (1973).
(3) Abbreviations: [14]dieneN₄ = 5,7,7,12,14,14-hexamethyl-1,4,8,-11-tetraazacyclotetradeca-4,11-diene; [14]tetraeneN₄ = 2,3,9,10-tetra-methyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene plus other abbreviations from ref 8 and 9.
(4) (a) D. P. Rillema, J. F. Endicott, and N. A. P. Kane-Maguire, *J. Chem. Soc., Chem. Commun.*, 495 (1972); (b) manuscript in preparation.

exchange rate for the Co([14]tetraeneN₄)(OH₂)₂³⁺–Co([14]tetraeneN₄)(OH₂)₂²⁺ couple to be at least 10⁶ larger than the comparable rate for the closely related couple with [14]dieneN₄ equatorial ligands, and these authors cited some limited spectroscopic evidence for stronger association of axial ligands in Co^{II}([14]tetraeneN₄)X₂ complexes than in Co^{II}([14]dieneN₄)X₂ complexes. Since both these cobalt(II) complexes are low spin,[5] the two couples provide a unique opportunity to investigate directly the correlation of inner ligand reorganizational barriers with the magnitudes of self-exchange rates for electron transfer reactions.[6]

[14]tetraeneN₄   [14]dieneN₄
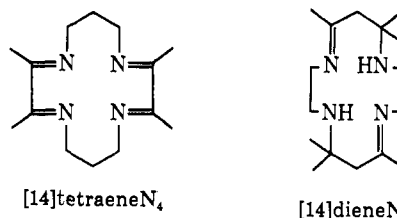
We are now able to report structural results for [Co([14]tetraeneN₄)(OH₂)₂] (ClO₄)₂ and [Co([14]tetraeneN₄)(NH₃)₂]Br₃ and can compare the reorganizational barrier based on these results to that inferred previously for the Co([14]dieneN₄)(OH₂)₂²⁺ couple. For the tetraene couple, the cobalt(II)–OH₂ bond distance is found to be 0.3 Å longer than the cobalt(III)–NH₃ distance. In both tetraene compounds all equatorial cobalt–N distances are equivalent indicating that the distortion is confined to the axial direction. Using Stranks' method,[7,8] and appropriate estimates of force constants,[8] we estimate an inner-sphere reorganizational energy of 7 ± 1 kcal/mol, significantly less than the similar barrier of 20 ± 1 kcal/mol estimated for the diene couple.[2] A difference of 14 kcal/mol is easily sufficient to account for the >10⁶-fold difference in self-exchange rates between the two couples. It has been noted[9] that the neglect of zero point and thermal vibrational energies leads to a slight overestimate of the reorganizational energy barrier when the above procedure is used. However, the correction should be comparable in both the diene and tetraene couples and thus does not significantly affect the value of the difference.

Several conclusions can now be drawn. First, the unusually slow cobalt(II)–cobalt(III) self-exchange for the diene couple results from an unusually large difference in bond lengths between the oxidized and reduced complexes. Second, the contributions of inner-sphere reorganizational barriers to the observed chemical re-

(5) Determined at 35° in 1 *M* NaCl solutions, μ_{eff} = 1.82 BM for ([14]tetraeneN₄)Co(II) and μ_{eff} = 1.86 BM for ([14]dieneN₄)Co(II).
(6) For pertinent reviews see (a) R. G. Linck, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci., Inorg. Chem.*, 9 (1), 303 1971; (b) A. G. Sykes, *Advan. Inorg. Chem. Radiochem.*, 10, 153 (1967); (c) H. Taube, "Electron Transfer Reactions of Complex Ions in Solution," Academic Press, New York, N. Y., 1970; (d) N. Sutin, "Inorganic Biochemistry," Vol. 2, G. L. Eichhorn, Ed., Elsevier, New York, N. Y., 1973, Chapter 19, p 611; (e) R. A. Marcus, *Annu. Rev. Phys. Chem.*, 15, 155 (1964); (f) W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer," Ronald Press, New York, N. Y., 1965.
(7) D. R. Stranks, *Discuss. Faraday Soc.*, 29, 116 (1960).
(8) For $r^{\pm} = (k_{II}r_{II} + k_{III}r_{III})/(k_{II} + k_{III})$, in which k_{II} and k_{III} are force constants for the cobalt(II)–OH₂ and cobalt(III)–OH₂ stretching vibrations, respectively. In the actual calculation we use $k_{II} \simeq 0.7 \times 10^5$ dyn cm⁻¹ and $k_{III} \simeq 1.7 \times 10^5$ dyn cm⁻¹ which are values for the respective cobalt–NH₃ vibrations and find $r^{\pm}$ = 2.05 Å. The total energy may then be derived from $E_{total} = k_{II}(r_{II} - r^{\pm})^2 + k_{III}(r_{III} - r^{\pm})^2$.
(9) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, 2nd ed, 1967, p 458.