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A New View of the Dynamics of Singlet Cis–Trans Photoisomerization

Sir:

Cis–trans photoisomerization around carbon–carbon double bonds has long been a subject of experimental investigation (see, for example, ref 1 and 2) and theoretical interpretation.[3-6] There is overwhelming evidence that singlet photoisomerization plays an important role in many systems, including the visual pigment; yet the dynamics of the process are not well understood. According to the customary viewpoint, radiationless transitions to the cis and trans ground states occur from a twisted "common intermediate" in which the vibrational energy levels are in thermal equilibrium.[3,4,7,8] This picture cannot describe cases when the lifetime of the twisted excited state is too short for vibrational equilibration[6,9] (see note 10). The semiclassical trajectory approach[5,6] might be more adequate for studies of the dynamics of cis–trans photoisomerization. Using this approach to study photoisomerization of alkenes and polyenes, we have found that *the surface crossing probability for a twisted double bond in its excited singlet state is much larger than previously thought, leading to a new dynamic picture of singlet cis–trans photoisomerization.*

Figure 1 shows typical ground and first excited singlet state potential energy surfaces as functions of the torsion angle ϕ of the isomerized bond. The photoisomerization process (Figure 2) involves excitation to the upper surface at $\phi \simeq 0$, rotation about the isomerizing bond to $\phi \simeq \pi/2$, oscillations in the excited state minimum, and surface crossing to the ground state with conservation of the sense of the torsional momentum.[6,11,12] The surface crossing probability per pass through the excited-state minimum is given[6] by

$$\theta = \left[\int_{\text{pass}} \dot{a}_0(t)\mathrm{d}t\right]^2$$

$$\int \dot{a}_0(t)\mathrm{d}t = \int a_1(t)\sigma(\phi)\dot{\phi}\exp\left\{-\frac{i}{\hbar}\int_0^t [E_1(\phi(t')) - E_0(\phi(t'))]\mathrm{d}t'\right\}\mathrm{d}\phi/\dot{\phi} \quad (1)$$

where $|a_i(t)|^2$ is the probability that the system is in the ith electronic state at time t and the initial conditions for the integration are $a_1(0) = 1, a_0(0) = 0$. ψ_i and E_i are the electronic wave function and adiabatic potential surface of the ith electronic state and $\sigma(\phi) = \langle\psi_1|\partial\psi_0/\partial\phi\rangle$ is the singlet–singlet nonadiabatic coupling. If θ is small, the quantum yield (Y) cannot be significantly greater than ½ (Figure 2). If θ is the same on each pass, then one obtains[13]

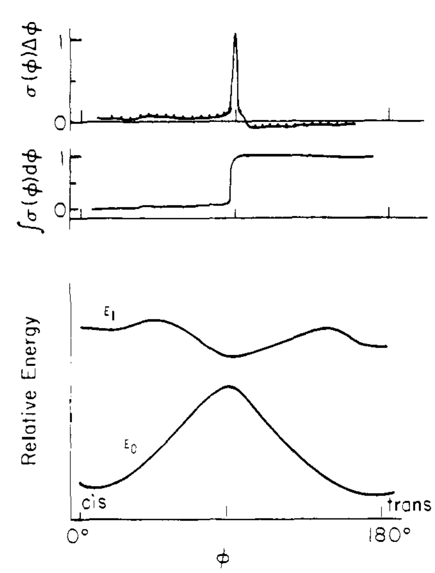

Figure 1. (Bottom) Energy diagram showing the ground and first excited singlet states of an alkene or polyene. E_0 and E_1 are the adiabatic energy surfaces as functions of the double-bond torsional angle ϕ. (Top) The nonadiabatic coupling between the two states, $\sigma(\phi)$, and its integral which determine the transition probability to the ground state. $\sigma(\phi)$ is presented multiplied by $\Delta\phi$ where $\Delta\phi$ is the increment used in numerical evaluation of $\sigma(\phi)$. These values of $\sigma(\phi)$ were calculated for rotation about the 11–12 bond of retinal.[13]

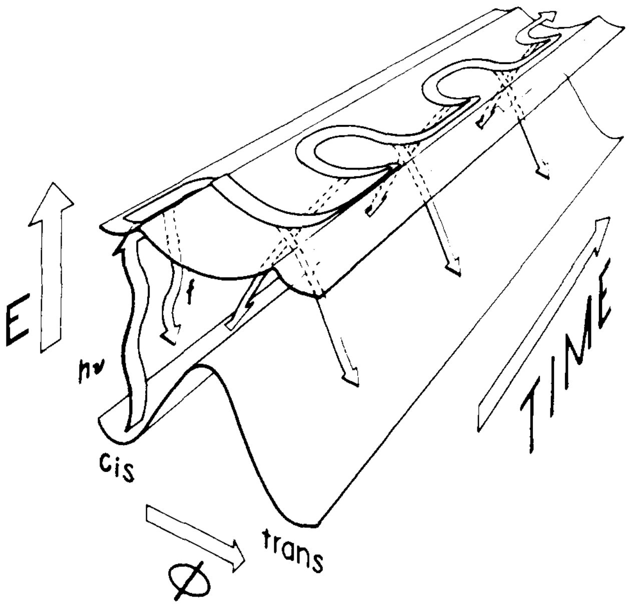

Figure 2. Photoisomerization dynamics in the region $\phi \simeq \pi/2$ showing the relationships between surface crossing probability and cis–trans quantum yield. The molecule oscillates in the excited-state torsional minimum. Transitions which occur while ϕ is increasing result in trans product, while decreasing, cis. If the transition probability per oscillation is small, many oscillations will take place in this region and the probabilities of crossing in each direction will be ~0.5. If the transition probability is large, more product than reactant will result from the molecules reaching this region. Note that some fraction (f) does not reach the crossing region.

$$Y = (1 - f)\theta[1 + (1 - \theta)^2 + (1 - \theta)^4 + \ldots] = (1 - f)/(2 - \theta) \quad (2)$$

where f is the fraction of molecules that never reach the crossing region owing to competing processes (e.g., fluorescence and radiationless transitions from the minimum at $\phi \simeq 0$).

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Typically the singlet-singlet coupling, $\sigma(\phi)$, is smaller than 0.1 deg^{-1} and this gives $\theta < 0.1$ which would lead (assuming nonzero f) to values of $Y < 0.5$. However, in double bonds which are asymmetric owing to distortion or substitution, there is an exceedingly large and narrow peak in σ (Figure 1).

This nonadiabatic dynamic coupling comes from instantaneous reversal of bonding and antibonding character exactly at $\phi = \pi/2$ and can be illustrated most easily in the Hückel approximation. Consider Löwdin orthogonalized p_z atomic orbitals λ_a and λ_b on atoms whose difference in ionization potential is ΔI and resonance integral is $\beta = \beta_0 \cos \phi$. In the range of ϕ in which $|\beta| \ll |\Delta I|$ the molecular orbitals are

$$\psi_+ = (\lambda_b + (\beta/\Delta I)\lambda_a)/[1 + (\beta/\Delta I)^2]^{1/2}$$
$$\psi_- = (\lambda_a - (\beta/\Delta I)\lambda_b)/[1 + (\beta/\Delta I)^2]^{1/2} \qquad (3)$$

Neglecting the small contributions from the normalization factor and the overlap of the Löwdin orbitals, we obtain, for $\phi \simeq \pi/2$ and $|\beta| \ll |\Delta I|$,

$$\sigma(\phi) = \langle \psi_+ | \partial \psi_- / \partial \phi \rangle \simeq -(1/\Delta I)(\mathrm{d}\beta/\mathrm{d}\phi) \simeq \beta_0 \sin \phi / \Delta I \qquad (4)$$

The angular range, ϵ, in which $|\beta| < |\Delta I|$ and eq 4 is valid, is given approximately by $|\epsilon| = |\Delta I/\beta_0|$. Since $\sigma([\pi/2] + \epsilon) \ll \sigma(\pi/2)$ we obtain (if ϵ is small enough so that the phase in eq 1 does not vary significantly in the region with large σ)

$$\theta \simeq \left[\int_{[\pi/2]-\epsilon}^{[\pi/2]+\epsilon} (a_1(\phi)\sigma(\phi)\mathrm{d}\phi)\right]^2$$
$$\simeq [\bar{\sigma}\, \bar{a}_1 \{(\cos([\pi/2] - \epsilon) - (\cos([\pi/2] + \epsilon)\}]^2 \simeq 0.5 \qquad (5)$$

where $\bar{a}_1$ and $\bar{\sigma}$ are the corresponding mean values of a_1 and σ in the range of integration. The peak in σ at $\phi = \pi/2$ persists in more refined calculations[13] using SCF/CI wave functions in the Pariser-Parr-Pople approximation corrected for overlap, the major change being to sharpen it to the point of being almost a δ function at $\phi = \pi/2$. This unexpected behavior of $\sigma(\phi)$ comes from the change in sign of coupling terms at this angle. It is still possible that this results from the instability that accompanies degenerate electronic surfaces,[14] but attempts to choose the slowest changing wave functions at $\phi = \pi/2$ did not change the behavior of σ.[13] Because of the narrowness of the peak in σ, θ does not depend on the energy gap between the surfaces.

The sudden increase in $\sigma(\phi)$ is related to the electronic instability that leads to the so-called "sudden polarization" at $\phi \simeq \pi/2$ of the excited-state charge distribution of twisted double bonds.[15] In large polyenes such as the visual pigment, $\sigma(\phi)$ changes much more quickly than the calculated charge distribution.[6]

The torsional oscillation frequency in the excited state at $\phi = \pi/2$, ν_p, and the excited-state lifetime in this region, τ_p, are related to θ by

$$\tau_p^{-1} \simeq \theta \nu_p \qquad (6)$$

τ_p can also be estimated using the observed Y where eq 2 and eq 6 give (for $Y > 0.5$)

$$\tau_p^{-1} \simeq (2 - (1 - f)/Y)\nu_p \qquad (7)$$

With $10^{12}\ \mathrm{s}^{-1} < \nu_p < 10^{13}\ \mathrm{s}^{-1}$ and $\theta \simeq 0.5$, we find that $2 \times 10^{-12}\ \mathrm{s} > \tau_p > 2 \times 10^{-13}$ s; this means that significant surface crossing occurs in a time which is too short to guarantee equilibrium in the twisted configuration of excited molecules. This is a major point of difference between the predictions of our approach and those of others, which predict a common intermediate between cis and trans species without considering the conservation of the direction of torsional momentum in the surface crossing process.[10] If $\theta \simeq 0$, the trajectory and common intermediate approaches merge.

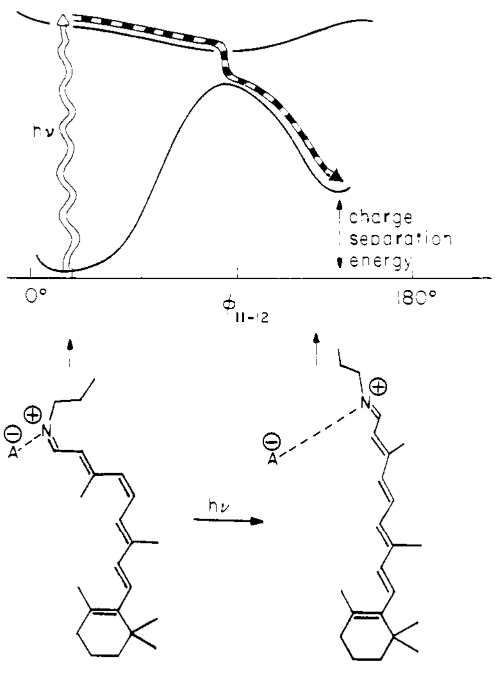

Figure 3. Photoisomerization as the first step of the vision process. Isomerization of the cis chromophore increases the distance between the protonated nitrogen of the Schiff base and a negatively charge protein group, thus storing electrostatic energy.[6,21] The actual active site is certainly more complicated; A^- in the diagram represents the electrostatic effect of the entire protein which probably results from a constellation of two acids and stabilizing dipoles that help to eliminate the excited-state barrier.[13]

An objection which might be raised to our treatment is how do we explain quantum yields less than 0.5? Referring to eq 2, we say that f is significantly greater than 0, and that many molecules do not reach the $\pi/2$ region; Y is therefore small.

Note the barrier in the excited state at $\phi \simeq 40°$. At 300 K a modest height of 4 kcal would trap excited molecules for approximately

$$\tau \simeq [10^{13} e^{-4/RT}]^{-1} \simeq 100\ \mathrm{ps} \qquad (8)$$

sufficient time to cross to the ground state on the side of reactants. The effect of such an excited-state activation barrier has been observed in stilbene, whose quantum yield depends on the temperature.[1,2]

Experimental evidence which we put forward in support of our ideas are (i) the nearly perfectly efficient photoisomerizations of both *cis*- and *trans*-cyclooctene;[9] (ii) the high quantum yield (0.67) and short reaction time (<6 ps) of the first step in the vision process;[6] (iii) the above-mentioned temperature dependence of the stilbene quantum yield; and (iv) every quantum yield observed to be equal to or greater than 0.5 in both directions.[2] Such quantum yields are incompatible with the existence of an equilibrated common intermediate (see eq 2 with $\theta \simeq 0$ and $f > 0$). On the other hand, systems in which $Y_{\text{cis-trans}} + Y_{\text{trans-cis}} \simeq 1$,[2,8] which we would have to attribute to coincidence,[19] are evidence for the common intermediate theories. If such intermediates exist,[16] it should be possible to decrease the excited-state lifetime significantly, and perhaps change the quantum yield by stimulating emission from the perpendicular excited state.

The high quantum yield of the first step of the vision process was considered the only serious problem in models involving cis-trans isomerization as the primary event.[20] It has been claimed, based on eq 2, that cis-trans models can account for the observed quantum yield only if θ is unusually large, while a model that involves "through-bond" charge separation[20,21] can account for the high quantum yield even if θ is small. Now it appears that θ is much larger than previously thought and therefore the high quantum yield is consistent with cis-trans isomerization as the primary event. Thus, if the present arguments about θ are not occasioned by mathematical artifacts, the first step of the vision process is likely to be a cis–trans photoisomerization reaction that can be described as a "through-space" charge separation[21] where the isomerization leads to separation of the positively charged Schiff base nitrogen and a negatively charged group of the protein[6,22] (Figure 3). The high quantum yield of the visual pigment indicates that the protein eliminates the excited-state barrier; this might involve proton transfer between two acids.[13]

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Catalysis of Hydrogen Production in Irradiated Aqueous Solutions by Gold Sols[1]

Sir:

In conjunction with the efforts to devise energy storage systems, it is often noted that many radicals which thermodynamically are capable of water reduction (or oxidation) to hydrogen (or oxygen) lack the kinetic stability to follow that course and would react via other pathways (such as disproportionation or dimerization) long before any detectable reaction with water occurs. Recent reports indicate, however, that redox catalysts may participate in the diversion of photochemically or thermally produced radicals or short-lived oxidation states of inorganic complexes from their energy-wasting back-electron-transfer reaction, dismutation, or dimerization reactions to the more profitable pathway of water decomposition.[2,3] Furthermore, it was recently shown by Henglein[4] that 2-propanol radicals will produce hydrogen in the presence of silver colloids rather than recombine. To this end we would like to present some results which indicate that aqueous solutions of gold sols may also serve as efficient catalysts for such a reaction.

Table I. Dose and Dose Rate Effect on $G(H_2)$ in the Aqueous 2-Propanol, Acetone, and Gold Sols

solutions[a]	dose rate, krad/min	dose, krad	$G(H_2)$[b]
c	1.55-16	7.75-32	1.10
	1.55	7.75	1.31
	1.55	10.85	1.65
	1.55	15.5	2.17
	1.55	31.0	2.62
d	1.55	31.0	1.05
	16	16	4.22
	16	24	3.94
	16	32	4.28
	16	48	4.43
d	16	32	1.02
	0.56	25.2	1.94[e]
	1.55	24.8	2.04[e]
	3.2	25.6	2.25[e]
	16	24	4.00[e]

[a] Unless otherwise stated deaerated 0.13 M 2-propanol and 0.13 M acetone, 5.4×10^{-4} M in Au and initial sodium citrate concentration of 3.9×10^{-3} M. [b] Molecular hydrogen yields in molecules/100 eV. Accuracy is ±0.1 G units. [c] As given in a without the gold and citrate components. [d] After coagulation and filtration of the gold. See ref 12. [e] For the sake of uniformity, these were normalized to a dose of 25 krad assuming linear dose dependence (<5% correction).

The 2-propanol radical in the present system was produced by γ-irradiation of aqueous solutions containing 0.13 M 2-propanol and 0.13 M acetone. The gold was chosen as the catalyst since the wealth of available information on these colloids[5] provides a means of production of the colloid under controlled conditions in a reliable, reproducible, and predictable manner. Furthermore, the size and shape of the gold colloids can be varied over a wide range.

In the above-mentioned solutions, reactions 1-4 will convert

$$H_2O \rightsquigarrow e_{aq}^- \ (G = 2.8),\quad H\ (G = 0.65),\quad OH\ (G = 2.8),\quad H_2\ (G = 0.45),\quad H_2O_2\ (G = 0.7) \qquad (1)$$

$$H + (CH_3)_2CHOH \rightarrow H_2 + (\dot{C}H_3)_2COH \qquad (2)$$

$$OH + (CH_3)_2CHOH \rightarrow H_2O + (CH_3)_2\dot{C}OH \qquad (3)$$

$$e_{aq}^- + (CH_3)_2CO \xrightarrow{H^+} (CH_3)_2COH \qquad (4)$$

all the radicals produced by γ-irradiation[6a] into the 2-propanol radical, thus producing a one-radical system.[6b] Although the latter radical has a low enough redox potential to reduce water to hydrogen,[7] such a reaction does not occur in homogeneous solutions and these radicals usually decay by a radical-radical dismutation of dimerization reaction.[8] As mentioned above, it was recently observed that silver colloids catalyze hydrogen production by this radical.[4] The yield of molecular hydrogen in the absence of the catalyst is therefore equal to $G_{H_2} + G_H = 1.1$. This was indeed found to be the case in our solutions also (in the absence of the catalyst) and was used in the latter experiments as the reference system.[9]

In Table I we summarize some of our results on the effect of the gold sols[10] on the hydrogen yield at different doses and dose rates. As can be seen in Table I, a substantial increase in