can laugh at the recent suggestion that the law of gravity be repealed "so everyone can get high," but what can we do when earnest humanists urge us to do all we can to prevent the building of nuclear power stations that "cause thermal pollution"? Is it suggested that we repeal, by consensus, the second law of thermodynamics?

The point is that, by insisting upon our "right" to reproduce, we have committed ourselves irrevocably to an ecological system that we hear little of —the complicated and delicately balanced technological clockwork that keeps us alive.

Ignorance of the law is no excuse. We have already heard too many cries of "but it was the *best* butter!" from overconfident tinkerers with the machinery. In a democracy, Everyman must be something of a scientist: he must know what is adjustable and what is deplorable.

The issue isn't a complicated one— either we, the scientific community, inform the general public; or the clock strikes 12.

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Highly Polarizable Singlet Excited States of Alkenes

The remarkable polar behavior of the first excited states of the double bonds in cyclohexenes and cycloheptenes discussed by Marshall (*1*) has an interesting explanation which leads to the prediction that singlet rather than triplet excited states will be found responsible.

A symmetrically substituted ethylene $R_2C = CR_2$ has geometrical symmetry group D_{2h} in its ground state. If the CR_2 groups are counterrotated about the double bond (assumed to be the x axis) the symmetry group is reduced to D_2, until the planes defined by the two CR_2 groups intersect at a 90° angle, when it becomes D_{2d} (*2*). In D_{2h} the lowest π orbital spans the b_{1u} representation, and the excited π^* orbital spans b_{2g}. These orbitals, respectively, correlate with b_1 and b_2 orbitals of the group D_2 appropriate to all angles of twist. However, in D_{2d} both orbitals span the same e representation (denoted $2e$).

Thus when the planes of the CR_2 groups become perpendicular, the two orbitals must become degenerate for reasons of symmetry. Even an infinitesimal perturbation can then force a finite change in the wave function if the perturbation contains a b_2 component in D_{2d}. In particular in the one-electron approximation, the presence of any electron-attracting or -repelling ion, molecule, or group near either end of the bond will produce an electric field that will mix the two e functions and cause a pronounced shift of electron density from one end of the bond to the other in a manner familiar from the Stark effect.

The two independent eigenfunctions of the Stark effect ψ_a, ψ_b are simply p orbitals, p_a on carbon atom a, and p_b on carbon atom b. The orbital p_a is perpendicular to the plane defined by its own CH_2 group; p_b is perpendicular to its CH_2 group. Thus p_a and p_b are perpendicular to each other.

One must therefore expect that, in any ethylenic system, a singly excited double bond will show a very marked increase in polarizability on twisting from the planar to the perpendicular conformation, if the Pauli principle does not force the two π electrons to occupy oppositely polarized e orbitals. On this basis one finds that it is the singlet ($^1A_1$, $^1B_2$) manifold rather than the triplet state which is unusually polarizable.

Kaldor and Shavitt have given an extensive discussion of the known data relative to perpendicular ethylene, and in particular have carried out all-electron LCAO SCF calculations (linear combination of atomic orbitals self-consistent field) [including configuration interaction (CI)] on the $^1A_1$ ($2e^2$) and $^1B_2(2e^2)$ states, which they find to be separated by only 0.1 ex (*2*, pp. 201–03). The greatest supposed separation of these states is that implicit in the diagrams of Merer and Mulliken who indicate that their energy 2.1 to 2.7 ev for the $^1A_1$ state is only a rough estimate (*3*). In contrast, the lowest states that could contribute appreciably to the polarizability of the $^3A_2$ state are the high-lying triplet Rydberg states (*4*). Now the $^1B_2$–$^1A_1$ Stark transition matrix element must be of the order (2.56 atomic units) eE where e is the electronic charge, E is the external electric field parallel to the $C = C$ bond, and 2.56 atomic units is the $C = C$ bond length in ethylene. A simple semiempirical LCAO perturbation calculation shows that even in the case of the 2.7-ev separation, the polarizability is very large. The field due to a charge of 0.1 e situated two $C = C$ bond lengths from the end of the twisted double bond causes a charge shift of 0.14 e from one C atom to the other. If the 0.1-ev separation is assumed, the corresponding shift is 0.999 e. This is of course a larger shift than one would find if one made an SCF calculation after including the Stark field in the Hamiltonian.

We conclude that, if a double bond is optically excited to the $\pi\pi^*$ singlet state and begins to twist, it will reach a highly polarizable configuration provided that transition to the triplet state does not occur. We propose therefore that it is the singlet rather than the triplet state that reacts ionically. It may be possible to find substituted ethylenes (such as cyclohexenes or cycloheptenes with heavy atom substituents) in which intersystem crossing is more rapid than the internal rotation of the excited state. If our hypothesis is correct photoionic reactions of such molecules would be inhibited, while if the triplet state is the active species, the opposite could be found to be true.

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References and Notes

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4. The $^3B_1$ states arising from the configurations $(1e)^3$ $(2e)^3$ and $(2e)$ $(3e)$ probably lie above all the states arising from the $(2e)^2$ configuration, and certainly are much above the ground $^3A_2\,(2e^2)$ state. In the LCAO-SCF-CI approximation these $^3B_1$ states contribute to the polarizability of the $^3A_2$ state in the x direction only through hyperconjugative mixing of the p_a orbital with $(CH_2)_b$ bonding or antibonding orbitals, and the corresponding mixing of p_b with such $(CH_2)_a$ orbitals.

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