Chemical Evidence of a Triplet Mechanism in the Photoisomerization of Nitrostilbenes. Formation of Singlet Oxygen from Triplet States of Nitrostilbenes

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Summary In the presence of oxygen several photoexcited ($\lambda > 300$ nm) *trans*-4-nitrostilbenes give rise to the formation of singlet excited oxygen whereas *trans*-stilbenes substituted by other groups as well as unsubstituted *trans*-stilbene do not.

ACCORDING to earlier work the *trans*$\rightleftharpoons$*cis* photoisomerization of unsubstituted stilbene[1] and of 4-cyano-4′-methoxystilbene[2] occurs *via* singlet states only whereas the *trans*→*cis* photoisomerization of 4-nitrostilbenes[2–4] proceeds *via* triplet states.

If this is correct the photochemical excitation of stilbene or 4-cyano-4′-methoxystilbene in the presence of oxygen in solution should not lead to the production of singlet oxygen O_2 ($^1\Delta g$) since there are no triplets present for quenching by ground state oxygen. Fluorescence quenching by oxygen is negligible under our conditions. However, excitation of nitrostilbenes which have been shown to yield triplet transients[3] quenched by oxygen with lifetimes of *ca.* 100 ns should give rise to singlet oxygen formation.‡

TABLE. Sensitization of the photo-oxygenation of α-terpinene in methanol by substituted *trans*-stilbenes

Sensitizer	v_{max}[a] /(ml O_2 min^{-1})	Relative quantum yield of $^1O_2$ formation
Stilbene	—	—
4-Chlorostilbene	—	—
4-Bromostilbene	—	—
4-Iodostilbene	—	—
4-Aminostilbene	—	—
4-Methoxystilbene	—	—
4-Hydroxystilbene	—	—
3-Nitrostilbene	0·017	0·06
4-Nitrostilbene	0·081	0·28
4,4′-Diaminostilbene	—	—
4-Nitro-4′-dimethylaminostilbene	—	—
4-Cyano-4′-methoxystilbene ..	—	—
4-Nitro-4′-methoxystilbene ..	0·071	0·24
2,4-Dinitrostilbene	0·063	0·22
4,4′-Dinitrostilbene	0·073	0·24
2,5-Dimethoxy-4′-nitrostilbene ..	0·085	0·30
Rose Bengal	0·229	0·8[7]

[a] Initial rate of oxygen consumption, 313 nm, 25 °C; reproducible by ⩽ ±0·005. [b] Relative to Rose Bengal, $\phi = 0{\cdot}8$ (283—373 nm) (refs. 6 and 7).

As a specific chemical indicator for singlet oxygen the α-terpinene system[5] was chosen. It is insensitive to light-induced autoxidation without the sensitizer and yields the 1,4-peroxide ascaridol as the single primary product. The rate of oxygen consumption was used as an approximate measure for the efficiency of $^1O_2$ production. Rose Bengal as an optimum sensitizer [ϕ ($^1O_2$) = 0·8][6,7] served as a standard. Ascaridol was independently detected by g.l.c. and t.l.c. in all cases when oxygen had been consumed.

Of the tested compounds shown in the Table only the nitrostilbenes sensitize singlet oxygen generation. Other stilbenes, including the highly polar 4-cyano-4′-methoxystilbene, gave no indication of $^1O_2$ formation. The quantum yield of $^1O_2$ with nitrostilbenes as sensitizers in methanol is *ca.* 0·2—0·3.

These findings confirm the previous conclusions concerning the triplet mechanism for the *trans*→*cis* photoisomerization of nitrostilbenes.[3] However, the question arises which triplet state induces the $^1O_2$ production. Only two triplet states are available which differ in their conformation: the lowest planar *trans* triplet state (tr^3) and the lowest twisted triplet state (p^3) (p for perpendicular). The difference between the energy of p^3 and of the twisted ground state (p^0) is too small to account for the value of 22·6 kcal mol^{-1} in the formation of $^1O_2$. [For *trans*-4-nitrostilbene, the triplet energy, E_T, is expected to be smaller than that of *trans*-stilbene, *i.e.* ⩽ 50 kcal mol^{-1},[8] the energy of activation E_a for the thermal *cis* → *trans* isomerisation is 34 kcal mol^{-1},[9] and $\Delta(\Delta H^\circ)$ between the isomers is 7 kcal mol^{-1};[10] thus $\Delta p = E_T - E_a - \Delta(\Delta H^\circ) \leqslant 9$ kcal mol^{-1}.] Therefore, only the tr^3 state can be the source of the required energy.

On the other hand oxygen efficiently quenches the triplet intermediate in the *trans*→*cis* isomerization of the nitrostilbenes[3] with no shift of the position of the photostationary state in benzene[3] or cyclohexane[11] and small shifts in polar solvents.[11]† It follows that oxygen must also quench the p^3 state. A thermal equilibrium between tr^3 and p^3 would account for these results.

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† For 4-nitro-4′-methoxystilbene a shift in ethanol was observed (G. Fischer and E. Fischer, *Mol. Photochem.*, 1974, **6**, 463) from $\phi(trans \rightarrow cis) = 0{\cdot}10$ (argon) to $\phi(trans \rightarrow cis = 0{\cdot}05$ (oxygen).

‡ In the photoisomerization of thioindigo dyes $^1O_2$ formation from triplet intermediates has also been observed (A. D. Kirsch, and G. M. Wyman, *J. Phys. Chem.*, 1975, **79**, 543).

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