# Xenon Perturbation as a Mechanistic Probe for the Involvement of Short-lived Triplets in Solution Photochemistry[1]

By Harry Morrison,* Thomas Nylund, and Fred Palensky
(*Chemistry Department, Purdue University, W. Lafayette, Indiana* 47907)

*Summary* Xenon perturbation is a useful tool for detecting triplet involvement in solution-phase photoreactions proceeding through non-quenchable triplet states.

Hammond and his co-workers recently reported[2] the use of bromocyclopropane as a method for enhancing solute intersystem crossing in solution and thereby determining whether photoproducts were singlet or triplet derived. Such a method is particularly useful when triplet precursors are so short-lived that quenchers are ineffective. Under such circumstances, increased triplet formation can be informative. Unfortunately, a whole class of substrates (the benzenoid aromatics) do not permit the use of bromocyclopropane because of the halide's absorption at wavelengths $<300$ nm. For such compounds, xenon represents the ideal alternative.[3]

Though xenon has been used in just this fashion in the gas phase,[4] its use in solution has been limited to a singlet-state reaction, where concomitant product and fluorescence quenching is observed.[5] We now report two examples of product enhancement, one involving a reaction having a hitherto uncharacterized excited state, which illustrate the power of the method. The data are summarized in the Table.

Table. Effect of xenon on several photochemical reactions in hexane solution[a]

| Substrate (reaction) | Conversion into product (xenon relative to argon) |
|---|---|
| 1-Phenylbut-2-ene (*cis-trans* isomerization) | 43% increase |
| 2-Methylenebenzonorbornene (photoisomerization) | 40% increase |
| 6-Phenylhex-2-yne (intramolecular cycloaddition) | 53% decrease |

[a] All irradiations at 254 nm and room temperature, using vacuum degassed solutions saturated with xenon or argon; data are averages of 2–4 measurements for each system. Xenon quenched the fluorescence of all three substrates by 40—60% in a separate set of experiments.

It may be seen that the previously postulated[6] triplet involvement for 1-phenylbut-2-ene isomerization is confirmed. Quenching studies had been useless for this molecule because of the very short triplet lifetime. 2-Methylenebenzonorbornene undergoes a 'diverted di-$\pi$-methane' reaction[7] and again, the triplet lifetime is too short for the triplet to be trapped. The xenon data now indicate a triplet precursor, a surprising result considering the presence of a 'free rotor' olefin. The final example (6-phenylhex-2-yne) is of a recently postulated singlet cycloaddition;[8] the decrease observed confirms both the validity of that proposal and the reliability of the procedure.†

It appears that xenon perturbation of solution-phase photoreactions deserves to be more routinely employed than it has in the past; it avoids the ambiguity of other reactive and/or light absorbing quenchers and is the method of choice for detecting the intermediacy of short-lived triplets.

(*Received*, 13*th October* 1975; *Com.* 1167.)

---

† One would normally expect quenching of reactions involving the singlet excited state; the reservation to be borne in mind is that if the triplet can successfully give the same product, and if $k^{T}_{pdt} > k^{S}_{pdt}$, enhancement rather than quenching will be observed. The ratio of these rates will likewise determine the response of a reaction proceeding simultaneously through both excited states.

[1] For previous paper in the series, 'Organic Photochemistry'; see: H. Morrison and O. Rodriguez, *J. Photochem.*, 1975, **3**, 471.

[2] R. H. Fleming, F. H. Quina, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1974, **95**, 7738.

[3] A. R. Horrocks and F. Wilkinson, *Proc. Roy. Soc.*, 1968, *A*, **306**, 257; A. R. Horrocks, A. Kearvell, K. Tickle, and F. Wilkinson, *Trans. Faraday Soc.*, 1966, **62**, 3393; R. B. Cundall and W. Trippett, *ibid.*, 1970, **66**, 350.

[4] See, for example, S. Y. Ho, R. A. Gorse, and W. A. Noyes, Jr., *J. Phys. Chem.*, 1973, **77**, 2609.

[5] R. B. Cundall and A. J. R. Voss, *Chem. Comm.*, 1968, 902.

[6] H. Morrison and R. Peiffer, *J. Amer. Chem. Soc.*, 1968, **90**, 3428; H. Morrison, J. Pajak, and R. Peiffer, *ibid.*, 1971, **93**, 3978.

[7] F. Scully, J. Grutzner, and H. Morrison, *J. Amer. Chem. Soc.*, 1973, **95**, 5100.

[8] W. Lippke, W. Ferree, Jr., and H. Morrison, *J. Amer. Chem. Soc.*, 1974, **96**, 2134.