Non-radiative Lifetime of Excited Singlet Penta-1,3-dienes from the Absolute Rate of a 5-3 Hydrogen Shift in the Vapour Phase

By Alain Delaby and Stéphane Boué*

(*Department of Organic Chemistry, Physical-Organic Chemistry Grouping, Free University of Brussels,* 50 *F. D. Roosevelt Ave.,* 1050 *Brussels, Belgium*)

Summary Irradiation of *trans*-penta-1,3-diene at 254 nm yields penta-1,4-diene as a photoproduct in the vapour but not in the condensed phase; Stern–Volmer treatment of this quenchable reaction allows the calculation of the absolute rate constant and the deduction of a lifetime of *ca.* 2×10^{-8} s for the lowest excited singlet diene.

Direct photolysis of penta-1,3-dienes in the condensed phase is known[1] to give rise to geometrical isomerization, to 1,4 electrocyclization, to 1,3 cyclization yielding 1,3-dimethylcyclopropene, and to dimers. When irradiation is performed in the vapour phase at medium to high pressures (50—600 Torr), three new compounds appear: pent-2-yne and isoprene (the normal products of thermal rearrangement of 1,3-dimethylcyclopropene[2]) and penta-1,4-diene. None of the species obtained at low pressure from bond cleavages of "hot" ground states[3] was observed here. This completely quenchable shift of hydrogen leading to penta-1,4-diene affords a unique probe into the decay mechanism of singlet excited conjugated dienes.

Table. Production of penta-1,4-diene as a function of the pressure[a] of added ethane

Ethane pressure (Torr)	33	60	84	154	303	571
Penta-1,4-diene (μmol/min $\times 10^3$)	19·8	12·7	9·8	6·1	3·7	2·1
Φ (penta-1,4-diene) ($\times 10^3$)	7·4	4·8	3·7	2·3	1·4	0·8

[a] Constant *trans*-penta-1,3-diene pressure = 25 Torr; cell temperature = 20°; cell volume = 347 ml; absorbed light intensity = $1 \cdot 6 \times 10^{18}$ quanta min^{-1} at 254 nm (reversed Hg line).

It has been demonstrated[1] that *cis*- and *trans*-penta-1,3-dienes in their lowest S_1 state are distinct entities which cannot be relaxed by a 90° twist about the C-3–C-4 bond, although calculations[4] have predicted that rotation of one terminal p_π orbital should stabilize the excited state. Since the O–O absorption band has not been assigned with certainty it is not yet known where the lowest excited singlet of the pentadienes lies nor are the structure and lifetime well established.[5] The failure of acyclic conjugated dienes to fluoresce suggests that the spectroscopic singlet decays rapidly to the ground state. This was supported by the value for the experimental lifetime ($<10^{-9}$ s) determined on quenching the formation of 1,3,3-trimethylcyclobutene from excited 2,4-dimethylpenta-1,3-diene in the vapour phase,[6] but the argument is weak since it can apply only to the *s-cis* conformers. It was suggested[7,8] that 1,3-dienes decay and/or isomerize *via* a transient methylenecyclopropyl 1,3-diradical (resulting from a 1,3 p_π bonding overlap) and that the singlet lifetime would be as short as the time required for a non-hindered bond rotation, thus preventing a *trans* (S_1) $\rightleftharpoons$ *cis* (S_1) equilibration.[1]

$$\mathrm{D} \xrightarrow{I_a} \mathrm{D}_n^{*}$$

$$\mathrm{D}_n^{*} \xrightarrow{k_1} \text{Penta-1,4-diene}$$

$$\mathrm{D}_n^{*} \xrightarrow{k_2} \mathrm{P}$$

$$\mathrm{D}_n^{*} + \mathrm{M} \xrightarrow{k_3} \mathrm{D}_0^{*}$$

$$\mathrm{D}_0^{*} \xrightarrow{k_4} \mathrm{D}$$

Scheme. D = *trans*-penta-1,3-diene; k_2 includes all unimolecular decay modes other than formation of penta-1,4-diene; M represents any molecule colliding with the excited state.

Our results on the penta-1,3- → -1,4-diene conversion throw new light on this problem. The results (see Table) obey the Stern–Volmer relationship $1/\Phi$ (penta-1,4-diene)

$= 12 + (3{\cdot}9 \times 10^4)$ l mol^{-1} [Ethane]. This is best accommodated by the kinetic sequence shown in the Scheme from which equation (1) can be derived.

$$1/\Phi(\text{penta-1,4-diene}) = 1 + k_2/k_1 + (k_3/k_1)[\text{M}] \qquad (1)$$

From this we obtain $k_2/k_1 = 11$ and $k_3/k_1 = 3{\cdot}9 \times 10^4$ l mol^{-1}. If we assume that vibrational quenching takes place at every collision† and using $(\sigma_D + \sigma_M)/2 = 4$ Å the simple gas kinetic theory gives $k_3 = 1{\cdot}66 \times 10^{11}$ l mol^{-1} s^{-1}. Therefore, the absolute rate constant, k_1, for the hydrogen shift has a maximum value of $4{\cdot}3 \times 10^6$ s^{-1} and the lower lifetime limit for the excited species yielding penta-1,4-diene is given by $\tau = 1/(k_1 + k_2) =$ *ca.* 2×10^{-8} s. This value is significantly larger than was previously estimated for the first spectroscopic singlet and suggests that the lowest excited singlet corresponds to a relaxed distorted configuration lying in an energy well‡ and which would not fluoresce. Recalling the suggestion[8] that the S_1 and S_0 energy profiles might be degenerate (or close to that) at a low lying point of the excited state along the co-ordinate of the 1,3-diene → methylenecyclopropyl 1,3 diradical transformation, it may be that this quasi-degenerate conformation is identical to the long-lived non-spectroscopic singlet. Hence, there is a need for caution when referring to the singlet lifetime of dienes since several excited species have to be distinguished (the *s-cis* and *s-trans* conformers, the spectroscopic, and the relaxed states) and the experimental figure will depend on the kind of process which is used to measure it.

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† This assumption can only give an overestimate of k_1 and the resulting lifetime is therefore a lower limit.

‡ Such a state is similar to the phantom singlet invoked by Saltiel *et al.*[5]

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