Direct Photolysis of the Penta-1,3-Dienes: Recognition of Wavelength-dependent Behaviour in Solution

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Summary The quantum yields for geometrical isomerisation and 1,4-cyclomerisation of *cis*- and *trans*-penta-1,3-dienes differ for excitation at 228·8 and 253·7 nm; this is explained by a change in the vibrational modes through which the molecules relax on the S_1 hypersurface.

Although wavelength effects in condensed-phase photochemistry were reported long ago,[1] it is only recently that Michl made it clear[2] that any nuclear configuration promoted on the S_1 hypersurface† by a Franck–Condon transition can *a priori* relax through any of its $3n - 6$ vibrational modes provided the initial energy content is large enough for overcoming barriers, in which case the molecule may possibly move anywhere on the hypersurface faster than it would thermally equilibrate with the surroundings. We report here on a remarkable instance of a wavelength dependence which is best explained in terms of a change (subject to an energy barrier) in the accessibility of S_1 funnels or valleys.

The irradiation of *cis*- or *trans*-penta-1,3-dienes in solution with 253·7 nm light is known to yield 3-methylcyclobutene, 1,3-dimethylcyclopropene, and the geometrical isomer as primary products,[3] their quantum yield of formation being characteristic of the starting isomer. In contrast to these results we have observed that when the 228·8 nm output of a cadmium lamp is selected for excitation, 3-methylcyclobutene or 1,3-dimethylcyclopropene could not be detected while $\Phi(cis \rightarrow trans)$ and $\Phi(trans \rightarrow cis)$ are substantially lowered; the data are given in the Table.‡

Admittedly a slight decrease in Φ(cyclobutene) could be due to a change in the ratio $\epsilon(s\text{-}cis)/\epsilon(s\text{-}trans)$ for the *trans*-penta-1,3-diene with wavelength but a comparison of the u.v. spectra of the *cis*-penta-1,3-diene (which exists essentially as the *s-trans* rotamer[3,4]) and of the *trans* isomer (which may contain as much as 3% of *s-cis* rotamer at 20 °C[5]) makes it unlikely that the differential proportion of rotamer being excited would account for the dramatic effect which is observed; further work is required to resolve this point unequivocally§ and we are currently investigating the ratio Φ(cyclobutene)/$\Phi(trans \rightarrow cis)$ for *trans*-penta-1,3-diene at wavelengths longer than 253·7 nm (i.e. in the tail of the absorption) where the rotamer's composition should have the opposite influence on Φ(cyclobutene) since the spectrum of the *s-cis* conformer, relative to that of the *s-trans*, is expected to be red-shifted.[6]

The decreased quantum yield for geometrical isomerisation and the absence of 1,3-dimethylcyclopropene at 228·8 nm cannot be reasonably accounted for by conformational considerations nor can it be explained by a better Franck–Condon factor since the energy gap between S_0 and S_1 has increased. Therefore we suggest that excitation at 228·8 nm populates the S_1 hypersurface at a nuclear configuration

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† As pointed out by Michl, if an upper state is initially involved the molecule will eventually come across the S_1 profile which we are considering here, except if it were to emit directly, a very rare event in solution.

‡ A U.S. Government report [U.S. Nat. Tech. Inf. Serv., From Govn. Rep. Announce, 1974, **74**(4), 75] recently alluded to a wavelength effect observed by G. S. Hammond in the pentadienes system but did not describe which kind of effect it is.

§ Professor O. L. Chapman has recently been able to analyse the changes, upon progressive heating,[7] in the u.v. spectrum of a high-temperature-equilibrated mixture of *s-cis* and *s-trans* butadienes frozen at 4 K in an argon matrix; we thank him for disclosing this information prior to publication.

TABLE. Quantitative influence of the exciting wavelength on the decay paths of the penta-1,3-dienes in spectrograde cyclohexane at 20 °C (1 cm quartz cells; magnetically stirred solutions). The diene concentration ranges from 10^{-1} to 1 mol l^{-1}; light intensity: $3{\cdot}97 \times 10^{-9}$ einstein s^{-1} cm^{-3} at 228·8 nm.[a]

Products	Starting diene			
	cis-Penta-1,3-diene		*trans*-Penta-1,3-diene	
Exciting wavelength	253·7[c]	228·8	253·7[c]	228·8
Quantum yields[b]				
cis-Penta-1,3-diene	—	—	0·083	0·022
trans-Penta-1,3-diene	0·100	0·025	—	—
3-Methylcyclobutene	0·003	0·000[d]	0·03	0·000[d]
1,3-Dimethylcyclopropene ..	9×10^{-4}	0·000[d]	19×10^{-4}	0·000[d]
Dimers	0·06[e]	0·064[f]	0·04[e]	0·044[f]

[a] ϵ(*cis*) = 31 at 253·7 nm; 17,900 at 228·8 nm and ϵ(*trans*) = 50·6 at 253·7 nm; 15,100 at 228·8 nm as determined on samples freshly purified by g.l.c. and using the Cd or Hg resonance lines for measuring the optical density of standard solutions. [b] All quantum yields correspond to initial conditions. [c] From ref. 3. [d] Undetectable. [e] Determined on a 4×10^{-1} mol l^{-1} solution. [f] Determined on a 10^{-1} mol l^{-1} solution.

which is displaced from the energy well reached at 253·7 nm and from where the molecules are driven by the slope of the surface into motions which no longer make use of 1,4 or 1,3 bonding overlaps as efficient modes for vibrational relaxation; one possible new relaxation mode involved here might well be that associated with a rotation about the C(2)–C(3) bond in the *s-cis* conformers as is suggested by the *s-cis* → *s-trans* photoisomerisation reported by Chapman.[7] Other vibrations need to be included in the picture for the *s-trans* conformers and we are presently testing the influence of the C–H vibrator by studying specifically deuteriated dienes.

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