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The wavelength dependence of the photochemistry of previtamin D

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Abstract

Dauben et al. (J. Am. Chem. Soc. 113 (1991) 8367) have found that the quantum yield of the photochemical electrocyclic ring closure of previtamin D changes dramatically within a very narrow wavelength range. Two conflicting models have been proposed as explanations: control by conformers, or an excited state effect involving the crossing of S_1 and S_2. We measured the spectrum of the less stable cZc conformer by matrix spectroscopy and showed that it caused only a minor wavelength dependence. However, the second model also disagrees with part of this dependence. We suggest another mechanism which seems to be consistent with all observations: ring closure competes with double-bond isomerization (the latter process has a barrier so that its rate depends on the photon energy). Analysis of the data yields the branching ratio of reaction to internal conversion. Surprisingly, it is different from that of ring opening. This may be due to the existence of an additional decay channel from excited previtamin D: single-bond isomerization to the other conformer. Further properties of the potential energy surfaces are discussed.© 1997 Elsevier Science S.A.

Keywords: Hot photochemical reaction; Conical intersections; Branching ratios

1. Introduction

Wavelength dependences in photochemistry [1] can be due to ground state factors or to excited state effects. The former are caused by species present in thermal equilibrium with the educt, e.g. different conformers or bimolecular complexes, if their spectra differ from that of the educt. In addition, secondary photoreactions of primary products can counterfeit a wavelength dependence. In this work, we ignore secondary reactions and complexes. However, a wavelength dependence of photochemistry can also result from the excitation of different electronic states if the population exchange between them is sufficiently slow. Except for very small molecules, such as iodine [2], this condition is usually met only if these states are well separated in energy [1]. The wavelength dependence observed in previtamin D was interpreted by one group on the basis of a postulated difference in conformer spectra [3,4], whereas another group invoked two different excited states ($1B_2$ and $2A_1$) [5]. The potential curves of these two states cross each other, and the population is transferred from the $1B_2$ to the $2A_1$ state probably in a time similar to that found for molecules such as hexatriene (10–60 fs [6,7]). Thus any competing process must be assumed to be extremely fast. In this work, we suggest that the smooth part of the wavelength dependence is caused by conformer control, whereas the sudden change in a narrow wavelength region is caused by an effect of a hot reaction in the excited state. One of the two competing reactions proceeds over a barrier in the excited state, so that its velocity increases with the excess energy, which depends on the excitation wavelength. A hot reaction competing with fluorescence has been reported [8].

1.1. Reaction scheme and previous models

Previtamin D is an open chain steroid triene which has basically two different conformers, denoted as P (tZc) and P_0 (cZc) in Scheme 1. (We ignore the fact that each of them can occur in two helical senses.) The room temperature spectra are shown in Fig. 1. Both of the conformers can undergo a photochemical Z–E isomerization to tachysterol (T, T_0). However, only the minor conformer (cZc) has a suitable geometry to yield photochemical electrocyclic ring closure to dehydrocholesterol (D) or, with the other helical sense of the conformer, to lumisterol (L). It was therefore natural to attribute the wavelength-dependent ratio $r(\lambda)/t(\lambda)$ of the ring closure yield divided by the Z–E isomerization yield to an assumed difference in the absorption spectra of the two conformers [3]. Support for this interpretation was deduced from model hexatrienes, in which the conformer composi-

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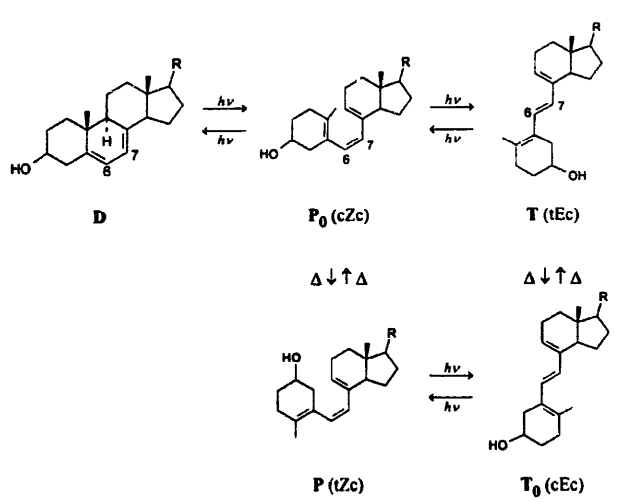

Scheme 1. Reaction scheme. The assignment of the reactions between the conformers is taken from Ref. [9]. According to Section 3, the P_0–P interconversion can occur not only thermally (Δ), but also photochemically.

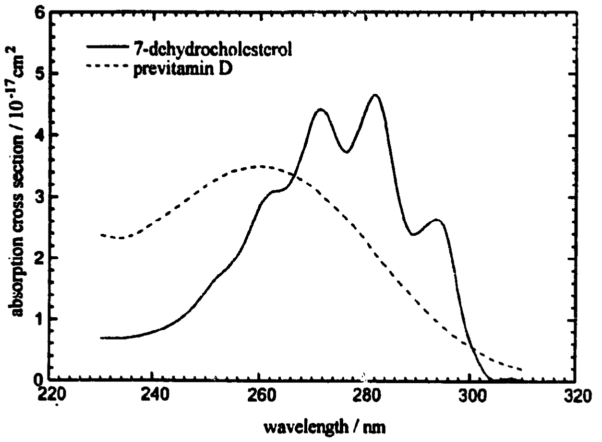

Fig. 1. Room temperature spectra of 7-dehydrocholesterol (D) and previtamin D (mixture of conformers P and P_0).

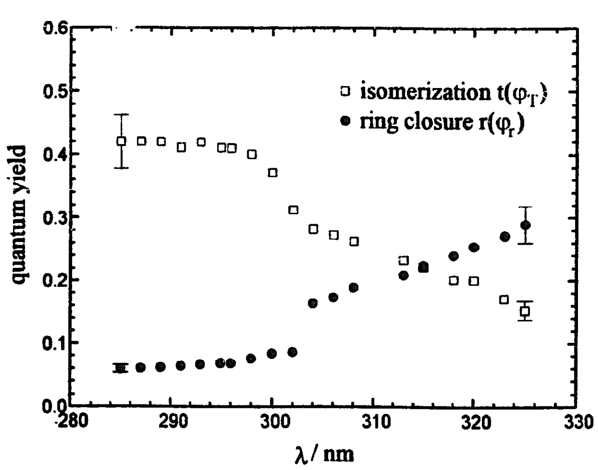

Fig. 2. Wavelength dependence of the quantum yields of ring closure and double-bond isomerization during the irradiation of previtamin D (mixture of P and P_0). The data are from Ref. [5].

tions were varied by varying the substituents [4]. On the other hand, careful studies of the quantum yields by Dauben et al. [5] showed a jump by a factor of two within the very narrow range between 302 and 305 nm (Fig. 2). It was argued that such a sudden change in the ratio of the absorption cross-sections is not conceivable for the two conformers, whose spectra are believed to be completely smooth. As an alternative, Dauben et al. [5] suggested that the sudden change occurs at the wavelength at which transitions to the ("bright") $1B_2$ state (S_2) and to the ("dark") $2A_1$ state (S_1) cross each other. They assumed that S_2 shows a fast loss to the ground state (S_0) by internal conversion, which competes with the conversion to S_1, and proposed that the photochemical processes originate only from S_1. They presented evidence indicating that the crossing is in fact located in the mentioned wavelength range. However, this mechanism predicts constant quantum yields at long wavelengths, which populate only S_1. The experiments show a strong, although smooth, quantum yield variation in this region [5].

We propose that the process competing with ring closure is double-bond isomerization, and that this process has a barrier leading to a dependence on the photon energy. This idea has already been suggested by Bernardi et al. [10], but has not been analysed further.

2. Experiments and results

In this work, we prepared the cZc conformer (P_0) of previtamin D by photochemical ring opening of 7-dehydrocholesterol (D) in a matrix at 91 K and measured its UV absorption in a conventional spectrometer. The irradiation was carried out in a 1 cm quartz glass cell, surrounded by a vacuum sleeve, by a pulsed, frequency-doubled dye laser at 295 nm. At this wavelength, the ratio of the absorption cross-sections $\sigma(D)/\sigma(P)$ (and probably also $\sigma(D)/\sigma(P_0)$) is at a maximum (cf. Fig. 1), so that the secondary photochemistry of P_0 should be minimized. The irradiation was repeatedly interrupted, with a small conversion in each step, and the spectrum was measured. For a preliminary evaluation, we subtracted from the measured spectra those of D and T (i.e. tachysterol, the secondary product which dominates after long irradiation), each multiplied by a factor such that the known vibrational structures of D and T disappeared. These factors yield the conversions and thus the concentrations of the products.

The resulting difference spectrum is the spectrum of cold P_0. It is shown in Fig. 3. This spectrum is shifted by only 3 nm to longer wavelengths compared with that of the normal tZc conformer (P) at a similar temperature. Both spectra are otherwise similar and are very smooth. More details of the spectra and the origin of the temperature shift will be discussed in later work [9]. The spectra show that the jump in the quantum yields cannot be explained by any spectral difference between the conformers. Since we have already pointed out the difficulties of the alternative model, we present here a different explanation.

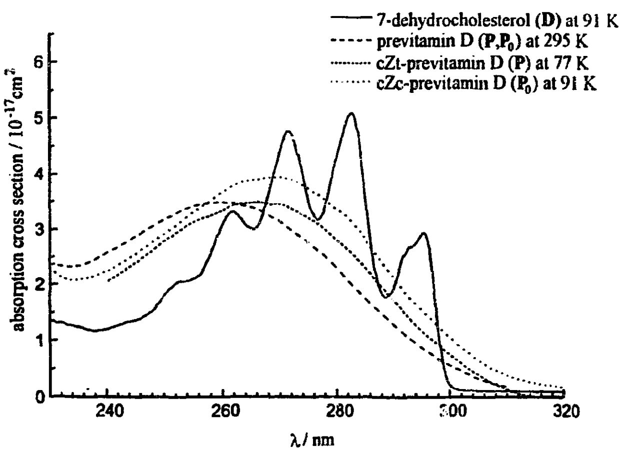

Fig. 3. Spectra of D at 91 K, P at 77 K, P_0 at 91 K and thermal previtamin D (mixture of P and P_0) at 295 K. The low-temperature spectrum of P is from Ref. [5]. In Ref. [5], the P–P_0 mixture was dissolved and cooled. P prevails at low temperature.

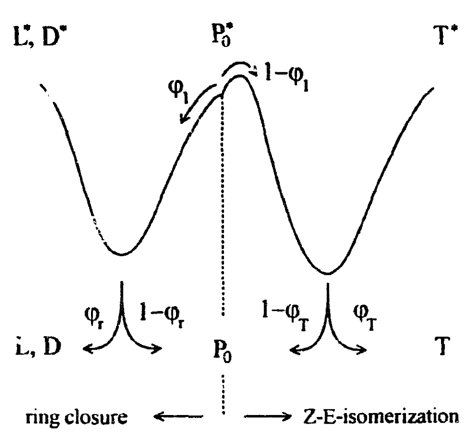

Fig. 4. Schematic diagram of the $2A_1$ potential energy surface with the suggested reaction pathways.

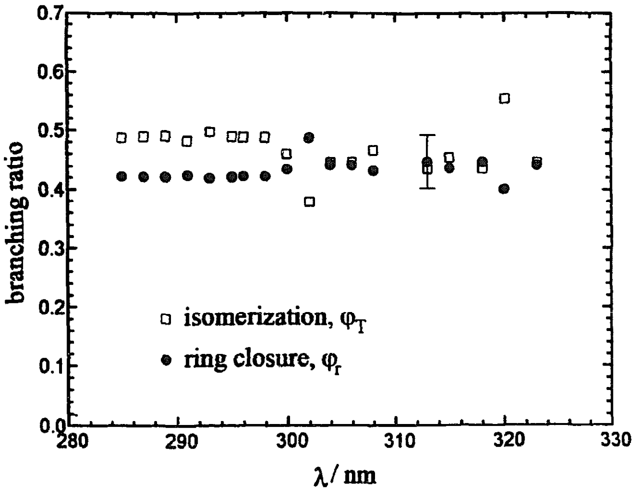

Fig. 5. Test of the model. φ_r and φ_T are wavelength independent in the range in which only P_0 absorbs ($\lambda \geq 300$ nm). For completeness, we also show the data below 300 nm, although the evaluation (Eqs. (1) and (2)) neglects the absorption by P. The evaluation according to Eqs. (1) and (2) requires a reference wavelength λ_{ref}; in this figure, we used $\lambda_{ref} = 325$ nm. Other choices of λ_{ref} generate slightly different sets of φ_r and φ_T, whose scattering is shown by the error bar.

3. Discussion

3.1. Model with a barrier in one of the competing reactions

Fig. 3 shows that, at wavelengths longer than about 310 nm, the absorption of P_0 is far larger than the absorption of P at 77–91 K. At 295 K, the spectra are shifted by about 10 nm, so that this limit is expected at 300 nm at room temperature. Therefore, in the region of the jump in the quantum yields, we will neglect the absorption of P and will concentrate on the photochemistry of P_0.

The basic assumption of the suggested model is that the path (Fig. 4) from excited P_0 branches (ratio $\varphi_1/(1-\varphi_1)$), leading to the ring closure valley without a barrier or, along another coordinate, to the Z–E isomerization valley over a small barrier; from each of the valleys (minima of the $2A_1$ surface), there is a path via another branching (conical intersection) leading to ring closure + educt (ratio $\varphi_r/(1-\varphi_r)$) or to educt + E isomer (T) (ratio $(1-\varphi_T)/\varphi_T$). The wavelength dependence reflects the dependence of $(1-\varphi_1)$ on the excess energy. All branching ratios can be deduced from the published data (Fig. 2) using

$$r(\lambda) = \varphi_1(\lambda)\varphi_r \tag{1}$$

$$t(\lambda) = (1-\varphi_1(\lambda))\varphi_T \tag{2}$$

where r and t are the measured quantum yields of ring closure and formation of tachysterol respectively (Fig. 2). For a given wavelength λ, there are three unknown and two measured quantities. Taking the data at a second λ, we can solve the equations for all φ. The data at the remaining wavelengths can be used to check the assumption of the model that φ_r and φ_T are λ independent. Fig. 5 shows that they are in fact constant in the range $\lambda \geq 300$ nm, where the P_0 absorption dominates. (The apparent outliers at 320 and 302 nm seem to be outliers in the original data (see the deviations from a smooth line especially in the sum of the quantum yields in Ref. [5], fig. 3).) The λ independence contrasts with the strong variation of the measured data (by a factor of five for $r(\lambda)$). This provides strong evidence that the model is at least partly accurate.

This agreement contrasts with the mentioned problems of the previous model [5] in this wavelength region. In Ref. [5], it was assumed that the λ dependence reflects the different probabilities of excitation of S_2 and S_1, that all the reactions occur only from the latter and that there is a rapid deactivation $S_2 \rightarrow S_0$ competing with the internal conversion $S_2 \rightarrow S_1$.

In this case, it is difficult to understand why the ratio of the products should depend on λ (internal conversion is a loss, affecting both products in the same way) and why the yields should depend on λ in a region which, according to Ref. [5], mainly S_1 is excited. The general assumption that the photochemical processes all start from the S_1 state is also not sufficiently detailed. According to the general view, also presented in Ref. [5], the minimum of S_1 is common to D and

P_0. If all processes started from this state, the product T (normally formed from P_0 or P) would also form from D. However, T is not a primary product of the photolysis of D [11]. The crucial feature of our model in this context is that it postulates two consecutive branchings.

3.2. Branching ratios

For both ring closure to D or L and ring opening of D or L, the rate-determining step is the transition from the S_1 minimum to a conical intersection, where the path branches to either the educt or the product [12]. The rates and branching ratio $\varphi_r(1-\varphi_r)$ should be the same for the forward and backward reactions. Table 1 compares this ratio for ring opening and ring closing. It also shows the analogous comparison for the Z–E and E–Z isomerizations. In contrast with expectation, φ_r in the line "P_0" is not equal to the value in the preceding line. Also the φ_T values in the lines "P_0" and "T" are different.

There are several conceivable explanations.

1. Contrary to the assumption, the rate-determining step may be different for ring closure and ring opening, and also for Z–E and E–Z isomerizations. For the former reactions, this idea would be in conflict with all concepts of photochemical pericyclic reactions [8]. However, the double-bond isomerization proceeds via two different S_1 minima and conical intersections in the forward and backward reactions, as concluded from recent work on unsubstituted hexatriene [15,16].
2. When leaving the S_1 minimum, the molecules still remember from where they originated, carrying a further part of the momentum. Similar effects have been found in different systems [17]. However, in our case, we would have to postulate that the memory lasts for 5.2 ps, the lifetime of the S_1 state [18]. Long before this the momentum and vibrational energy will be redistributed.
3. In the first branching, there may be another channel which increases the internal conversion to the P_0 ground state. Such a channel has been found for several polyenes [19] and for hexatriene [16], and for the latter has also been predicted by ab initio calculations [15]. Single-bond isomerization occurs which, via a conical intersection, leads partly to the other conformer, but partly back to the starting conformer [15]. Fig. 6 shows the suggested two branchings, starting from P_0^* and T*, and indicates the rate constants in the direction of electrocyclic ring closure (k_{cl}) and of single- and double-bond isomerizations (k_{s} and k_{d}).

Table 1
Branching ratios for ring closure/ring opening and Z–E isomerization/E–Z isomerization, the reactions starting from an assumed common excited intermediate of educt and product (local S_1 minimum). The average in the third line is given for comparison with the back reaction, since the corresponding helical forms of P_0 have an abundance ratio of 1 : 2 (line P_0 is from this work; other data from [13,14])

Educt	$\varphi_r/(1-\varphi_r)$	$\varphi_T/(1-\varphi_T)$
D	0.66/0.34	–
L	0.58/0.42	–
(D+2L)/3	0.61/0.39	–
P_0	0.44/0.56	0.44/0.56
P	–	0.48/0.52
T	–	0.90/0.10

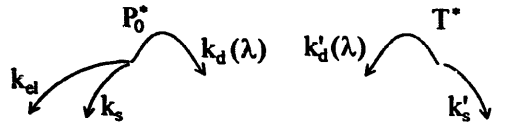

Fig. 6. Modified branchings for excited P_0 and T, including single-bond isomerization.

This refined model leads to the replacement of φ_{l} and $(1-\varphi_{\mathrm{l}})$ in Eqs. (1) and (2) by

$$\varphi_{\mathrm{cl}}=k_{\mathrm{cl}}/(k_{\mathrm{cl}}+k_{\mathrm{s}}+k_{\mathrm{d}}(\lambda)) \tag{3}$$

and

$$\varphi_{\mathrm{d}}=k_{\mathrm{d}}(\lambda)/(k_{\mathrm{cl}}+k_{\mathrm{s}}+k_{\mathrm{d}}(\lambda)) \tag{4}$$

respectively. To obtain a branching ratio for ring closure in agreement with ring opening (average of D and L as educt, with twice higher weight for L, in accordance with the weights for the helical forms making ring closure), we must postulate $k_{\mathrm{s}}/k_{\mathrm{cl}}=\varphi_{\mathrm{s}}/\varphi_{\mathrm{cl}}=0.39$. In a similar way for tachysterol (excited at 254 nm), we would have to assume $k'_{\mathrm{s}}/k'_{\mathrm{d}}=4.6$; however, as mentioned, for this case we doubt the existence of a common minimum for the forward and backward reactions, so that this latter ratio has no meaning.

3.3. Excess energy dependence and barrier

The evaluation above not only delivers the wavelength-independent φ_r and φ_T, but also $\varphi_{\mathrm{l}}(\lambda)$. Since

$$(1-\varphi_{\mathrm{l}}(\lambda))/\varphi_{\mathrm{l}}(\lambda)=\varphi_{\mathrm{d}}(\lambda)/\varphi_{\mathrm{cl}}(\lambda)\propto k_{\mathrm{d}}(\lambda) \tag{5}$$

this function reflects the energy dependence of k_{d}, the double-bond isomerization rate. It is plotted in Fig. 7 vs. λ^{-1}, the wavenumber of excitation. At a threshold of 33 000 cm^{-1} (303 nm), k_{d} makes a jump and tends to an asymptotic value at higher energies, as expected for a threshold process. At lower wavenumbers, k_{d} depends exponentially on the energy of excitation. This is probably due to the Boltzmann distribution of the molecules after excitation. To understand this, we should note that the (thermal) energy of the many UV-inactive modes is not affected by the excitation, so that their vibrational energy content is transferred to the upper electronic state. On the other hand, an energy of E_{act} in a UV-active mode will cause a certain shift Δ in the absorption. A red shift of the excitation by Δ will therefore reduce the vibrational energy by $(\Delta-E_{\mathrm{act}})$ to below the thermal value. Therefore the excitation wavenumber (abscissa in Fig. 7) correlates with the average vibrational energy content in the upper state, which in turn influences the rate k_{d} of overcoming the barrier. If the distribution of this energy is exponential (Boltzmann), k_{d} will (below the threshold) also depend exponentially on the excitation wavenumber. Therefore we

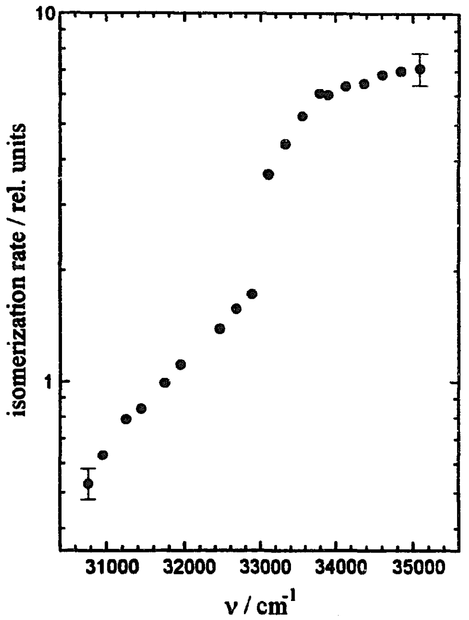

Fig. 7. Dependence of $(\varphi_1^{-1} - 1)$ on the wavenumber of excitation. This function reflects the excess energy dependence of the rate k_d for the double-bond isomerization channel. The asymptotic value at high energies is only qualitative, since P absorption is not negligible in this region, but has not been taken into account.

consider that Fig. 7 nicely confirms our model. It should be noted that the previous models provide no explanation for any wavelength dependence in this region.

Above 33 000 cm^{-1}, the barrier crossing k_d can compete efficiently with k_{cl} as well as with any cooling rate. The latter is probably of the order of 10^{11} s^{-1} and k_{cl} may be faster than 10^{12} s^{-1}. To be so fast, the barrier crossing needs a certain excess energy. Therefore the maximum of the barrier is probably slightly (by several k_BT) below 33 000 cm^{-1}, measured from the ground state. However, we cannot give the barrier height in the excited state, since the energy of the S_1 minimum is not known. It is probably more than 0.5 eV below the Franck–Condon region [12].

3.4. *The tZc conformer of previtamin D*

Dauben et al. [5] also measured the fluorescence of previtamin D and its temperature dependence. At 16 K, they reported a lifetime of 2 ns and a quantum yield of 0.18. This obviously cannot be attributed to P_0, since this molecule disappears from its S_1 minimum within a temperature-independent time of 5.2 ps [18]. The emission spectrum is different from that of the conceivable products T, D or L [20]. Therefore this fluorescence must be due to P, the tZc conformer of previtamin D.

At temperatures above about 80 K, the fluorescence yield strongly decreases. This dependence has been assigned to a competing process with a barrier height of 630 cm^{-1} [5]. It can be assumed that this process is double-bond isomerization (k_d), leading to a tachysterol conformer (to T_0 according to Ref. [9]). Then the process competing with fluorescence (radiative rate, 0.09 ns^{-1} [5]), even at 16 K, can be the channel (rate k_s) to a conical intersection, which leads to single-bond isomerization and internal conversion. k_s is calculated to be $(2\ ns)^{-1} - 0.09\ ns^{-1} = 0.49\ ns^{-1}$. It must be barrierless due to the low temperature. It is interesting to note that, in the unsubstituted counterpart of P, 1,3Z,5-hexatriene, these two processes have been identified with rates and activation energies similar to those above [16]. The small rate $k_s = 0.49\ ns^{-1}$ for P contrasts with the value for P_0, where it is probably faster than 0.1 ps^{-1}, since it can compete with the very fast ring closure ($k_r > 1/5.2$ ps, predicted from ring opening) and the vibrational cooling rate. This contrast is again consistent with observations on hexatrienes, where a slight modification of the molecule changes the barrierless rate by orders of magnitude [21].

Franck–Condon analysis of the fluorescence places the S_1 minimum at 29 600 cm^{-1} [5]. (This value may still depend on the interpretation of the temperature shift of the spectrum.) Adding to it the activation energy, we can expect that the tachysterol quantum yield will decrease dramatically below 30 200 cm^{-1} (331 nm). However, this is difficult to check since P shows practically no absorption in this region.

4. Conclusions

We believe that sufficient evidence has been presented for the two main claims of our model, i.e. that the reactions of excited P_0 proceed via two consecutive branching points and one of the competing channels, double-bond isomerization, has an early barrier which is responsible for the wavelength dependence of the process. This type of excited state effect has not often been observed; we only know of the case of Dewar-naphthalene, in which a hot reaction competes with fluorescence [8]. Obviously, hot reactions can work only if they are faster than the cooling rates. A hot double-bond isomerization can also probably be invoked for the similar observations in other trienes studied recently by Dauben et al. [22].

In recent experiments in a matrix (90 K), we found that a slight increase in the irradiation wavelength from 295 to 297 nm results in a very dramatic decrease in tachysterol formation, while maintaining ring closure and single-bond isomerization. Obviously, the matrix increases the barrier height by about 800 cm^{-1} compared with that in the liquid phase at room temperature. Such matrix effects are easily conceivable.

It is the general view that ring opening and ring closing have a common rate-determining step [8]. This theory would be confirmed if their branching ratios $\varphi_r/(1-\varphi_r)$ were the same for the forward and backward reactions. The fact that they are different (Table 1) is nevertheless compatible with this view, since a reasonable third channel (single-bond isomerization) can be postulated for the first branching point. A better check for a common intermediate would involve a comparison of the rate for ring closing with the rate for ring opening.

Evidence was found that, in 1,3,5-hexatriene, there are two different rate-determining steps for the photochemical Z–E and E–Z isomerizations [15,16]. We also assume that the $P_0 \rightarrow T$ and $T \rightarrow P_0$ rearrangements have different intermediates. Therefore our model provides no evidence on whether excited T can also isomerize around a single bond. Nevertheless, the existence of such an additional channel is suggestive for T, in analogy with P_0, P and the smaller hexatrienes [15,16].

Our analysis of the wavelength dependence yields a number of new features of the potential surfaces responsible for the electrocyclic ring closing and opening. One is the early branching (near the Franck–Condon region) of the reaction path. This branching is far above (by at least several k_BT) the S_1 minimum, since it is out of reach for the thermal energy. (For example, T cannot be formed by direct reaction from D, and D cannot be formed from T.) The curves of Fig. 4 are (schematic) cross-sections of the potential surfaces. Obviously, there is no low-energy path around the central barrier with the first branching. It is also worth noting that the early branching (in particular, the $Z \rightarrow E$ channel) has so far not been found by quantum chemical calculations [23], although the Z–E path has been found in other conformers [15].

In these curves, we omitted a commonly known detail, since it was unimportant for the model: the S_1/S_2 crossing. Except at very long wavelengths, the absorption populates the S_2 ($1B_2$) state [5]. From there, the molecule very rapidly (rate $k_{ic} > 10^{13}$ s^{-1}, see Section 1) crosses to the S_1 ($2A_2$) state, proceeding to the S_1 minimum and from there to a conical intersection and the products. The early branching postulated by us could take place in the S_2 state. In this case, the rates k_{cl} and k_d must compete with the rapid $S_2 \rightarrow S_1$ crossover. Therefore it is probable that (most of) the branching occurs in the $2A_2$ state.

Acknowledgements

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References

[1] For a survey, see N.J. Turro, V. Ramamurthy, W. Cherry, W. Farneth, Chem. Rev. 78 (1978) 125–145.
[2] Y. Zhang, W. Fuß, K.L. Kompa, J. Photochem. 23 (1983) 311–318.
[3] H.J.C. Jacobs, J.W.J. Gielen, E. Havinga, Tetrahedron Lett. 22 (1981) 4013–4016; H.J.C. Jacobs, Pure Appl. Chem. 67 (1995) 63–70, and references cited therein.
[4] A.M. Brouwer, J. Cornelisse, H.J.C. Jacobs, Tetrahedron 43 (1987) 435–438.
[5] W.G. Dauben, B. Disanyaka, D.J.H. Funhoff, B.E. Kohler, D.E. Schilke, B. Zhou, J. Am. Chem. Soc. 113 (1991) 8367–8374, and references cited therein.
[6] M.O. Trulson, G.D. Dollinger, R.A. Mathies, J. Chem. Phys. 90 (1989) 4274–4281.
[7] W. Fuß, T. Schikarski, W.E. Schmid, S. Trushin, K.L. Kompa, Chem. Phys. Lett. submitted for publication.
[8] M. Klessinger, J. Michl, Lichtabsorption und Photochemie Organischer Moleküle, Verlag Chemie, Weinheim, 1989.
[9] W. Fuß, S. Lochbrunner, A. Müller, W.E. Schmid, IUPAC Conference on Photochemistry, Helsinki, July 22–26, 1996.
[10] F. Bernardi, M. Olivucci, M. Robb, Israel J. Chem. 33 (1993) 265–276.
[11] H.J.C. Jacobs, E. Havinga, Adv. Photochem. 11 (1979) 305–373.
[12] P. Celani, S. Ottani, M. Olivucci, F. Bernardi, M.A. Robb, J. Am. Chem. Soc. 116 (1994) 10 141.
[13] S. Gliesing, M. Reichenbächer, H.-D. Ilge, D. Fassler, Z. Chem. 29 (1989) 21.
[14] H.J.C. Jacobs, J.W.J. Gielen, E. Havinga, Tetrahedron Lett. 22 (1981) 4013.
[15] M. Olivucci, F. Bernardi, P. Celani, I. Ragazos, M.A. Robb, J. Am. Chem. Soc. 116 (1994) 1077–1085. P. Celani, M. Garavelli, S. Ottani, F. Bernardi, M.A. Robb, M. Olivucci, J. Am. Chem. Soc. 117 (1995) 11 584–11 585.
[16] W. Fuß, T. Schikarski, W.E. Schmid, S. Trushin, K.L. Kompa, P. Hering, J. Chem. Phys. submitted for publication.
[17] B.K. Carpenter, Acc. Chem. Res. 25 (1992) 520–528.
[18] W. Fuß, T. Höfer, P. Hering, K.L. Kompa, S. Lochbrunner, T. Schikarski, W.E. Schmid, J. Phys. Chem. 100 (1996) 921–927.
[19] A.M. Brouwer, H.J.C. Jacobs, Rec. Trav. Chim. Pays-Bas 114 (1995) 449–458.
[20] E. Havinga, R.J. de Kock, M.P. Rappoldt, Tetrahedron 11 (1960) 276–284.
[21] W.J. Buma, B.E. Kohler, K. Song, J. Chem. Phys. 94 (1991) 6367–6376.
[22] W.G. Dauben, B. Zhou, J.Y.L. Lam, to be published.
[23] P. Celani, S. Ottani, M. Olivucci, F. Bernardi, M.A. Robb, J. Am. Chem. Soc. 116 (1994) 10 141–10 151.