J. CHEM. SOC. PERKIN TRANS. II 1985 1073

Rotational Barriers in Pentadienyl and Pent-2-en-4-ynyl Radicals

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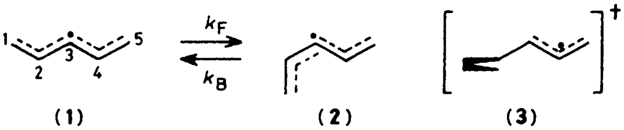
The barrier to internal rotation about the C(2)–C(3) bond in pentadienyl radicals was measured by line-shape analysis of the e.s.r. spectrum in the temperature range 320—420 K. The energy difference between the *trans*- and *cis*-conformers of pent-2-en-4-ynyl radicals was obtained from the temperature variation of their equilibrium concentration ratio and the barrier to interconversion was determined by e.s.r. line-shape analysis in the range 375—450 K. The rotational barriers and the corresponding stabilisation energies were in good agreement with previous estimates.

Pentadienyl radicals were observed by e.s.r. spectroscopy in 1979[1,2] and shown to exist in two planar conformations; the *E,E*- or W-form (**1**) and the *E,Z*- or Z-form (**2**). Rotation about the C(2)–C(3) partial double bond interconverts the two delocalised conformers. In the transition state (**3**) which corresponds to a 90° rotation the unpaired electron is confined to an allyl moiety of the pentadienyl system and the delocalisation is partially lost. The stabilisation energy E_s of pentadienyl radicals (also resonance or delocalisation energy) is therefore related to the barrier to rotation about the C(2)–C(3) bond E_i and the allyl stabilisation energy[2,3] as shown in equation (1), where V_2 is the very small, but experimentally

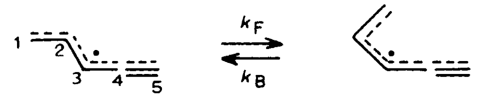
$$E_i = V_2 + E_s(\mathbf{1}) - E_s(\text{allyl}) \qquad (1)$$

inaccessible, barrier to rotation about the C(2)–C(3) *single* bond in the absence of delocalisation. The rotational barriers E_i can be determined in favourable cases by e.s.r. measurements of the concentrations of the two species in the temperature range where isomerisation occurs.[4,5] In the case of pentadienyl radicals difficulties with the synthesis of precursors which would yield only (**1**) or (**2**) initially,[3] and the fact that only conformer (**1**) could be detected at $T > 210$ K, meant that the rotational barrier could be only roughly estimated from the temperature at which (**2**) began to isomerise to (**1**).[2,3] Pentadienyl radicals are important models for more complex acyclic π-delocalised radicals and a more accurate determination of E_i was therefore desirable.

The situation was similar for the related five π-electron pent-2-en-4-ynyl radicals. Both the *trans*-conformer (**4**) and the *cis*-conformer (**5**) had been observed by e.s.r. spectroscopy.[6] The kinetics of their interconversion by rotation about the C(2)–C(3) bond had been investigated. In this paper we report the rotational barrier in W-pentadienyl radicals and new determinations of the rotational barriers in Z-pentadienyl and pent-2-en-4-ynyl radicals which were made using the potentially very accurate e.s.r. exchange line-broadening method.[7,8]



(**1**) (**2**) (**3**)



(**4**) (**5**)

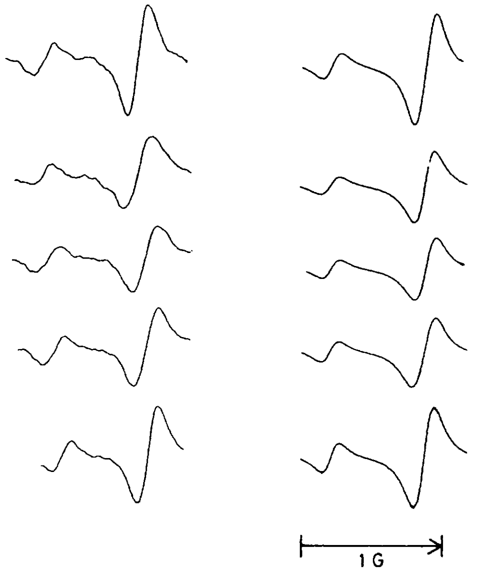


Figure 1. Portion of the 9.4 GHz e.s.r. spectrum of pentadienyl radicals: left, experimental spectra, from the top 322 K, 353 K, 375 K, 397 K, and 428 K; right, computer simulations, from the top $10^{-6}k/\text{s}^{-1}$ 5.0, 25.0, 50.0, 90.0, and 250

Results

Pentadienyl Radicals.—Pentadienyl radicals were generated in the cavity of the e.s.r. spectrometer by photolysis of penta-1,4-diene and di-t-butyl peroxide dissolved in t-butylbenzene. In agreement with previous work, only the spectrum of the W-conformer (**1**) could be detected at temperatures above ambient. We showed[3] that the Z-conformer (**2**) isomerises to the W-conformer at temperatures above 210 K. A possible reason for the absence of the Z-conformer in the spectrum at higher temperatures is that the W-conformer does not isomerise back to the Z-conformer in the accessible temperature range. This implies an unexpectedly large energy difference between the two conformers; it is more likely that at higher temperatures the two are in equilibrium but that the concentration of (**2**) is simply below the limit of detection of the spectrometer.

At *ca.* 320 K the spectrum showed selective line broadening which reached a maximum at about 370 K, the lines becoming sharp again by 420 K. The sample lifetime was short at the higher temperatures and it was not practicable to record the whole spectrum. A small portion of the spectrum, comprising the most intense line (low-field component) and its immediate low field neighbour, was scanned slowly at each temperature and some samples are shown in Figure 1. We attribute this

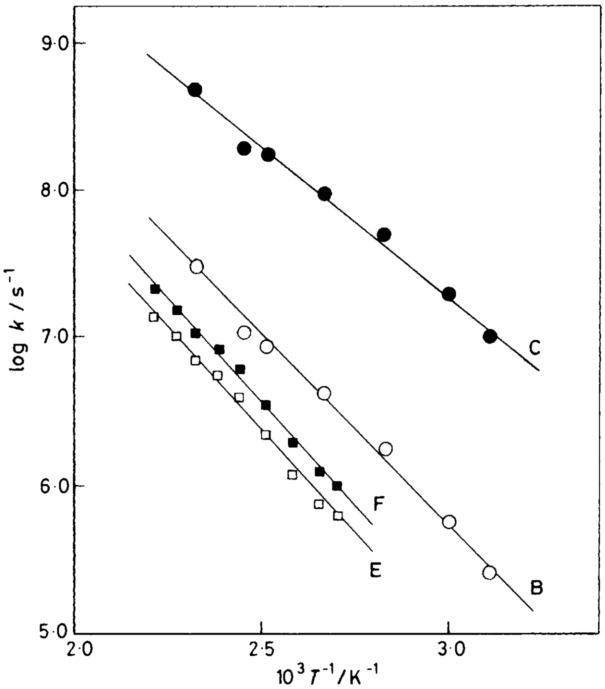


Figure 2. Arrhenius plots of exchange rates for pentadienyl and pent-2-en-4-ynyl radicals: line B (open circles) k_F(pentadienyl); line C (filled circles) k_B(pentadienyl); line E (open squares) k_F(pent-2-en-4-ynyl); line F (filled squares) k_B(pent-2-en-4-ynyl)

broadening to the onset of rotation about the C(2)–C(3) bond; the extent of the broadening was not large and the *average* spectrum at $T > 420$ K was not greatly different from that of the W-conformer because of the small proportion of the Z-conformer present at equilibrium.

The hyperfine splittings of the two conformers (**1**) and (**2**) were known already[1,2] and therefore the barrier to rotation could be determined by computer simulation and comparison of the calculated broadening for various exchange rates with the experimental spectra at different temperatures. In this case, however, the molar fractions of the two conformers had to be estimated at each temperature. From simulations with a variety of concentration ratios we found that satisfactory agreement with experiment at coalescence (*ca.* 370 K) could only be achieved for $[(\mathbf{1})]/[(\mathbf{2})] = K(370) = 25 \pm 5$. The temperature variation of $[(\mathbf{1})]/[(\mathbf{2})]$ was then obtained by assuming a linear plot of $\log[(\mathbf{1})]/[(\mathbf{2})]$ gainst $1/T$ through the above value and the origin [*i.e.* equal concentrations of (**1**) and (**2**) at infinite temperature]. Simulations made with a modified version of Heinzer's program[9] are shown in Figure 1; the corresponding rate constants (k_F and k_B) are set out in Arrhenius form in Figure 2. Least-squares treatment of the data yielded equations (2) and (3),* the error limits on the *A*-factors being estimated

$$\log k_F/\mathrm{s}^{-1} = (13.4 \pm 0.6) - (11.7 \pm 0.5\ \mathrm{kcal\ mol^{-1}})/2.3\,RT \quad (2)$$

$$\log k_B/\mathrm{s}^{-1} = (13.4 \pm 0.6) - (9.3 \pm 0.5\ \mathrm{kcal\ mol^{-1}})/2.3\,RT \quad (3)$$

from the spread on the Arrhenius plots. The fact that the calculated *A*-factors were close to the 'normal' value for bond rotation of 10^{13} s^{-1} increases confidence in the reliability of the rotation barriers.

Table 1. Measured concentration ratios for *trans*- (**4**) and *cis*-(**5**) pent-2-en-4-ynyl radicals

T/K	$[(\mathbf{4})]/[(\mathbf{5})]$	T/K	$[(\mathbf{4})]/[(\mathbf{5})]$
280	1.95	325	1.67
293	1.92	336	1.67
295	1.87	346	1.55
304	1.89	357	1.56
314	1.75	365	1.58

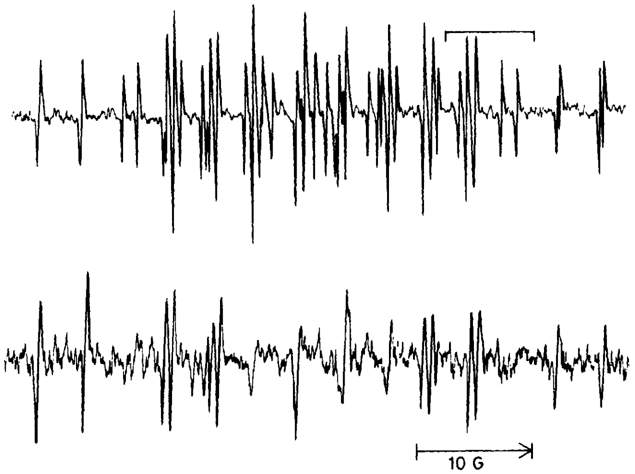


Figure 3. E.s.r. spectra (9.4 GHz) of pent-2-en-4-ynyl radicals: upper spectrum at 250 K, lower spectrum at 420 K; bracketed region on the upper trace is shown on an expanded scale in Figure 4

Pent-2-en-4-ynyl Radicals.—Pent-2-en-4-ynyl radicals were generated in the cavity of the e.s.r. spectrometer by photolysis of pent-1-en-4-yne and di-t-butyl peroxide dissolved in hexadecane. Hydrogen abstraction by t-butoxyl radicals from the different conformers of pent-1-en-4-yne produced both the *trans*-(**4**) and *cis*-(**5**) radicals, which could be distinguished in the e.s.r. spectrum (Figure 3). We showed previously[6] that the two radicals interconvert at $T > 280$ K, and hence the equilibrium concentration ratio $[(\mathbf{4})]/[(\mathbf{5})] = K = k_F/k_B$ was measured at several temperatures from the intensities of suitable peaks in the spectra of each radical. The data are given in Table 1; least squares treatment (including the origin) gave equation (4).

$$\log[(\mathbf{4})]/[(\mathbf{5})] = (-0.009 \pm 0.02) + (0.37 \pm 0.05\ \mathrm{kcal\ mol^{-1}})/2.3\,RT \quad (4)$$

Exchange line-broadening was observed in the temperature range 375—450 K, with coalescence at *ca.* 430 K. The full spectrum at 420 K with many of the lines extensively broadened is compared with the slow exchange spectrum in Figure 3. Sample boiling prevented observation of the fast exchange limit at $T > 450$ K. A portion of the spectrum (see Figure 3) was scanned slowly at each temperature and then matched with computer simulated spectra. The hyperfine splittings of the two conformers in the slow exchange limit were taken from previous work;[6] careful calibration of the magnetic field showed, however, that each splitting should be increased by 3.3%. The equilibrium ratio $[(\mathbf{4})]/[(\mathbf{5})]$ at each temperature during exchange broadening was obtained by extrapolation from the Arrhenius line [equation (4)]. Some samples of the fits are

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* 1 cal ≡ 4.18 J.

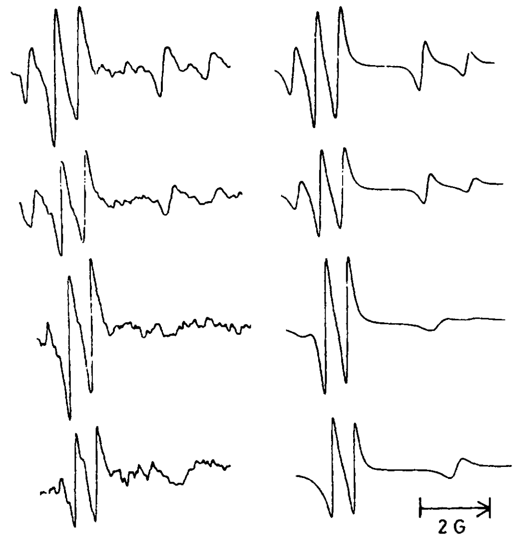
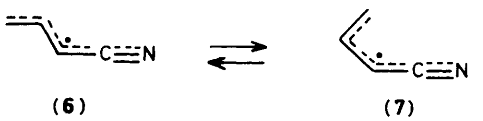


Figure 4. Portion of the e.s.r. spectrum of pent-2-en-4-ynyl radicals: left, experimental spectra, from the top 376 K, 386 K, 418 K, and 450 K; right, computer simulations, from the top $10^{-6}k/s^{-1}$ 1.0, 1.6, 7.0, and 20.0



(6) (7)

shown in Figure 4; the rate constants are given in Arrhenius form in Figure 2. Least squares treatment yielded equations (5) and (6).

$$\log k_F/s^{-1} = (13.5 \pm 0.6) - (13.0 \pm 0.4\ \text{kcal mol}^{-1})/2.3\,RT \quad (5)$$

$$\log k_B/s^{-1} = (13.5 \pm 0.6) - (12.7 \pm 0.4\ \text{kcal mol}^{-1})/2.3\,RT \quad (6)$$

In an attempt to determine the rotational barrier in 1-cyanoallyl radicals the *trans*- (**6**) and *cis*- (**7**) conformers were generated by hydrogen abstraction from allyl cyanide in hexadecane. The spectra and hyperfine splittings were essentially the same as those described previously.[4] A portion of the spectrum was scanned at temperatures up to 470 K but this was found to be still below the coalescence temperature. Measurements at higher temperatures were impracticable because of sample boiling and decomposition and the line-shape analysis could not be applied in this case.

Discussion

The W to Z equilibrium constant of 25 ± 5 at 370 K for pentadienyl radicals leads to a free energy difference of 2.4 ± 0.2 kcal mol^{-1} between the two conformers. This is virtually identical with the difference in their enthalpies of formation as given by the difference in the activation energies of the forward and reverse isomerisations; *i.e.* the W-conformer is found to be 2.4 kcal mol^{-1} lower in energy than the Z-conformer. This difference seems quite reasonable in comparison with known analogies. Thermochemical data suggest that *trans*-alkenes are *ca.* 1 kcal mol^{-1} more stable than *cis*-alkenes.[10] Semi-empirical SCFMO calculations of the enthalpies of formation of the pentadienyl conformers are in good agreement. Thus, INDO calculations predict the W-conformer to be 2 kcal mol^{-1} lower in energy;[2,3] MINDO/3 calculations with complete geometry optimisation[11] predict a difference in $\Delta H_f°$ values of 1.0 kcal mol^{-1}. We have also carried out calculations using the UHF version of the MNDO program[12] and find, for the optimised structures, a difference of 1.0 kcal mol^{-1} in their enthalpies of formation.

Table 2. Barriers to rotation in delocalised radicals

Radical	Method	Barrier E_i/kcal mol^{-1}	Ref.
Allyl	SSK[a]	15.7 ± 1.0	*c*
W-Pentadienyl (**1**)	EB[b]	11.7 ± 0.5	This work
Z-Pentadienyl (**2**)	EB	9.3 ± 0.5	This work
Z-Pentadienyl (**2**)	SSK	8.9	3
Z-Pentadienyl (**2**)	SSK	6—7	2
trans-Pent-2-en-4-ynyl (**4**)	SSK	11.8 ± 2	6
trans-Pent-2-en-4-ynyl (**4**)	EB	13.0 ± 0.4	This work
cis-Pent-2-en-4-ynyl (**5**)	SSK	11.4 ± 2	6
cis-Pent-2-en-4-ynyl (**5**)	EB	12.7 ± 0.4	This work
Heptatrienyl	SSK	≤8.5	13

[a] Steady state kinetic method. [b] Exchange line broadening method. [c] H.-G. Korth, H. Trill, and R. Sustmann, *J. Am. Chem. Soc.*, 1981, **103**, 4483.

The barriers to rotation in pentadienyl radicals are compared with previous determinations in Table 2. The value of E_i for Z-pentadienyl radicals found by the exchange-broadening method is within experimental error equal to the estimates from steady-state kinetic studies. The barrier for W-pentadienyl radicals has not been determined before, but our experimental value is close to previous estimates[13,14] and, as expected, lies between the rotational barriers of allyl and heptatrienyl radicals (Table 2). The more accurate E_i from the present work means that the stabilisation energy (E_s^{esr}) for W-pentadienyl radicals should be slightly increased to 25 kcal mol^{-1}.

The value of E_s(pentadienyl) has also been determined thermochemically from measurements on the heat of formation of pentadienyl radicals.[15–17] The thermochemical stabilisation energy of a radical R• is defined as the difference between the C–H bond dissociation energy in RH and that of a non-delocalised model compound (MH) [equation (7)]. When

$$E_s = DH°(MH) - DH°(RH) = \Delta H_f°(M^\bullet) - \Delta H_f°(MH) - [\Delta H_f°(R^\bullet) - \Delta H_f°(RH)] \quad (7)$$

secondary alkyl radicals are chosen as the model species this procedure gives *ca.* 18.5 kcal mol^{-1} as the thermochemically derived resonance energy.[15–17] However, as pointed out by Dewar[18] and others[3] this procedure has the disadvantage that secondary alkyl radicals are themselves strongly stabilised by hyperconjugative/inductive effects (10.0 kcal mol^{-1} for isopropyl[15]). Pentadienyl radicals will also be stabilised by hyperconjugative/inductive effects, but to a lesser extent because they have fewer β-hydrogen atoms than the model species. It follows that stabilisation energies calculated in this way overcompensate for the inductive/hyperconjugative contribution and thus underestimate the true 'resonance energies.' Alternatively, E_s can be defined relative to methyl radicals as the model species, thus giving E_s^{MeH}(pentadienyl) = 28.7 kcal mol^{-1}. The methyl radical is not stabilised by hyperconjunction/induction and thus the E_s^{MeH} value contains no compensation for these effects. We would expect therefore that E_s^{esr} derived from the barrier to rotation should lie between these two thermochemical estimates, and this is indeed the case.

For pent-2-en-4-ynyl radicals the difference in the activation energies of the forward and reverse isomerisations indicates that the *trans*-conformer (**4**) is 0.3 kcal mol^{-1} lower in energy than the *cis*-conformer (**5**); this is in excellent agreement with the value of 0.37 kcal mol^{-1} derived from equation (4). MINDO/3 calculations predict an energy difference of 0.5 kcal mol^{-1} between (**4**) and (**5**).[6] In Z-pentadienyl radicals (**2**) there is an unfavourable steric interaction between the *syn*-hydrogen atom on C(1) and that on C(4). In *cis*-pent-2-en-4-ynyl radicals (**5**) this steric effect is absent and hence the *trans*- and *cis*-conformers of this radical are closer in energy than those of pentadienyl radicals. The rotational barriers for (**4**) and (**5**) derived from the exchange-broadening experiments agree with those determined previously by steady state kinetics (Table 2) to within experimental error. The present results suggest a small increase (*ca.* 1.0 kcal mol^{-1}) in the stabilisation energies of (**4**) and (**5**). Overall, the exchange-broadening results confirm the pattern of delocalisation established for polyenyl and other delocalised radicals[13,14] and put the correlation of E_s^{esr} with the radical hydrogen hyperfine splittings on a firmer footing.

Experimental

E.s.r. spectra were obtained with a Bruker ER200 D spectrometer. Samples were made up in Spectrosil quartz tubes, and degassed several times by freeze-pump-thaw cycles; *ca.* 0.9 atm. of He was then introduced before sealing and irradiating with light from a 500 W high-pressure Hg lamp. At higher temperatures (>420 K) thermal decomposition of the di-t-butyl peroxide was sufficiently rapid to make photolysis unnecessary.

Penta-1,4-diene and allyl cyanide were obtained commercially and used without purification; di-t-butyl peroxide was purified as described previously.[6] Pent-1-en-4-yne was prepared from ethynylmagnesium bromide and allyl bromide in tetrahydrofuran and purified by preparative g.l.c.[6]

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Received 3rd *October* 1984; *Paper* 4/1713