Iodine and Nitric Oxide Catalyzed Isomerization of Olefins. VII. The Stabilization Energy in the Pentadienyl Radical and the Kinetics of the Positional Isomerization of 1,4-Pentadiene[1]

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Abstract: The kinetics of the iodine atom catalyzed isomerization of 1,4-pentadiene to form 1,3-pentadiene has been studied in the gas phase over a temperature range from 129 to 241°. The formation of small amounts of *n*-pentenes and cyclopentene does not change the basically very simple rate law for the positional isomerization of *n*-pentadienes which is governed by the rate of abstraction of a hydrogen atom from 1,4-pentadiene (k_1) by iodine. The Arrhenius plot of the rate constant (l. mole^{-1} sec.$^{-1}$) for this process yields with standard errors: $\log k_1 = (9.15 \pm \pm 0.15) - (9.60 \pm 0.25)/\theta$, with $\theta = 2.303RT$ in kcal./mole. When compared with the activation energy for the analogous hydrogen abstraction from *n*-pentane, assuming the activation energies for the back reactions to be equal (HI attack on pentyl and pentadienyl radicals), one obtains 15.4 ± 1 kcal./mole for the resonance energy in the pentadienyl radical. This value is only 25% larger than the allyl stabilization energy. These stabilization energies are discussed in terms of a simple model of three-electron bonds and related to energies in the benzene system.

The nature and size of the resonance or stabilization effects is of broad general interest. In previous papers[2] a reliable value for the allyl stabilization energy in the 1-buten-2-yl radical has been reported to be 12.6 ± 1 kcal./mole, based on kinetic studies of the iodine catalyzed isomerization of 1-butene. Stabilization energies are defined as the difference in dissociation energies between a C–H bond in the unsaturated molecule under discussion and the similar C–H bond in the parent saturated paraffin at the same temperature.

After the successful measurement of the allyl stabilization energy, it was very tempting to try to apply the same method to diene hydrocarbons, both linear and cyclic. This paper reports on the results obtained using 1,4-pentadiene as a starting material which yields a stabilized conjugated open chain dienyl radical. Similar kinetic studies are presently being carried out, using cyclohexadienes, which should yield the C–H bond strength and the stabilization energy in cyclic dienyl radicals. All these data, together with the benzyl resonance energy,[3] should give a more complete and consistent picture of the character and nature of these stabilization energies in olefins. It was expected that the lowering of C–H bond dissociation energies by the generation of stabilization energies in the radical intermediates should be the same for linear and cyclic compounds.

While the iodine catalyzed positional isomerization of *n*-butenes showed well-behaved kinetics with only minor amounts of side products, the studies using diolefins revealed a number of possible side reactions which restricted the temperature range and catalyst pressure that could be used.

The most prominent side reactions are (1) the formation of *n*-pentenes through the four-center addition of HI to the conjugated diene, and (2) the cyclization of the pentadienyl radical intermediate. (3) The radical-initiated dimerization of the 1,3-pentadiene formed in the system[4] proved to be unimportant under the experimental conditions used. The relatively small contribution from side reactions as well as the dominant isomerization of 1,4-pentadiene were shown to be very surface sensitive. The only way to obtain homogeneous reaction rates was to coat the Pyrex vessels with Teflon. A method for "teflonizing" glass reaction vessels has been described previously.[5]

Experimental Section

A. Materials. 1,4-Pentadiene was obtained from Aldrich Chemical Co., Inc., Milwaukee, Wis. It was 99% pure, the main impurities being cyclopentene and *trans-* and *cis*-1,3-pentadiene. Resublimed iodine was used.

B. Procedure and Apparatus. The method and experimental setup have been described in great detail previously.[6] In short, the study consisted of measuring iodine, manometrically and photometrically, into the reaction system. At time zero, 1,4-pentadiene was added. Pressure changes measured using a pressure-transducer and changes in iodine concentration measured by light absorption were followed during the reaction. The reaction was quenched after a measured length of time by opening a stopcock to a system of collection traps. Iodine and high-boiling materials were retained in the first trap, kept at −15°. HI was absorbed in the next two traps, filled with glycine, before the C_5 fraction of the hydrocarbons was condensed over liquid nitrogen. After vaporization, pressure–volume–temperature measurements yield the balance of C_5 products when compared with the initial amount of 1,4-pentadiene. The kinetic runs were carried out in two equivalent Pyrex glass vessels, one of which was packed with glass tubing. The packed vessel had an 18-fold larger surface-to-volume ratio than the unpacked one. Both vessels were coated with Teflon as previously described.[5]

C. Analysis. Analysis of the product was carried out on a Model 720 F and M gas chromatograph, using a 20-ft. 0.25-in. column filled with firebrick (mesh 60/80) with a 20% coating of Dow Corning silicone oil 710. The column was operated at 30° with a He flow rate of 60 cc./min. The following retention times in minutes after the air peak were measured: *n*-pentane, 12.5;

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[1] This work has been supported in part by Grant No. AP-00353-01 from the U. S. Public Health Service Air Pollution Division to Stanford Research Institute.

[2] (a) K. W. Egger, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 5420 (1964); (b) S. W. Benson, A. N. Bose, and P. Nangia, *ibid.*, **85**, 1388 (1963).

[3] (a) G. L. Esteban, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 3873 (1963); (b) S. J. Price, *Can. J. Chem.*, **40**, 1310 (1962); (c) R. Walsh, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, **87**, 4053 (1965).

[4] J. B. Harkness, G. B. Kistiakowsky, and W. H. Mears, *J. Chem. Phys.*, **5**, 682 (1937).

[5] K. W. Egger and S. W. Benson, *J. Am. Chem. Soc.*, **87**, 3314 (1965).

[6] D. M. Golden, K. W. Egger, and S. W. Benson, *ibid.*, **86**, 5416 (1964).

Table I. Kinetic Data for the Positional Isomerization of 1,4-Pentadiene

								Product distribution[g,d]					
Temp.,[a] °K.	Time, min.	$[I_2]_0$,[b] torr	$[I_2]_f$,[b] torr	$[K_{I_2}]^{1/2}$[c] $\times 10^5$ torr$^{1/2}$	$[PD_{1,4}]_0$,[d] torr	C_5 material balance[e] loss, % $[PD_{1,4}]_0$[d]	Δp,[f] torr	$[PD_{1,3} + P_2 + P_c]/[PD_{1,4}]_f$	$100[P_2]/[PD_{1,3}]$	$100[P_c]/[PD_{1,3}]$	t/c, $PD_{1,3}$	k_1,[g] mm.$^{-1}$ min.$^{-1}$	k_1^{corr},[h] mm.$^{-1}$ min.$^{-1}$
402.4	244	23.7	23.7	0.1770	59.9	6.7	0.7	0.0455	24.3	9.5	4.12	21.2[i]	25.2
(3.42)	72	49.9	. . .		95.0	17.3	9.0	0.0243	420	153.5	1.90	26.7[i]	98.5
	104	24.5	. . .		55.6	16.7	3.2	0.0315	398	155.0	. . .	34.0[i]	69.0
422.3	42	17.2	. . .	0.5164	82.1	8.2	0.3	0.0509	13.2	16.2	5.55	37.1	55.3
(3.21)	91	10.9	. . .		45.3	. . .	0	0.0627	7.7	7.7	5.19	39.2	. . .
	194	13.0	. . .		34.0	13.5	1.3	0.1476	13.9	6.2	5.47	38.1	48.8
429.3 p	30	13.0	13.0	0.7362	101.6	3.1	0.2	0.0413	8.4	3.4	4.94	51.3[i]	51.3
p	91	4.9	4.3		114.9	2	0.6	0.1035	8.0	. . .	6.37	66.4[i]	66.4
(3.15)p	148	6.5	6.1		62.5	5.9	0.6	0.1783	7.1	. . .	5.78	58.9[i]	58.9
p	158	8.1	7.9		75.6	8.8	0.8	0.1952	10.2	. . .	5.44	53.7	64.5
451.4	28	19.2	. . .	2.114	85.4	11.2	1.1	0.1899	9.3	2.7	5.24	67.2	76.8
	29	13.9	. . .		136.8	10.0	0.6	0.1733	7.5	1.7	5.09	69.8	79.4
(2.97)	44	7.6	. . .		340.4	10.6	0.7	0.1953	6.9	1.9	4.31	69.6	79.0
	21	24.0	. . .		82.2	14.9	0.3	0.1366	8.4	2.4	4.97	59.0	80.2
461.5 p	10	8.3	8.3	3.293	157.2	2.8	0.3	0.0855	5.4	. . .	5.17	85.6	85.6
p	15	8.8	7.8		88.8	4.8	0.3	0.1242	3.8	. . .	5.50	81.9	81.9
(2.89)p	45	3.5	3.5		90.2	6.6	0.3	0.3050	2.6	0.1	4.34	94.2	100.1
p	16	15.9	15.0		26.2	10.7	0.1	0.1596	2.7	. . .	5.65	71.0	75.2
464.3	25	7.7	7.6	3.703	90.9	10.3	0.6	0.2469	5.8	0.6	5.44	85.1	93.2
	30	3.9	. . .		68.4	7.7	0.1	0.2348	2.9	0.3	4.36	96.7	102.1
(2.87)	47	2.1	1.6		40.3	8.9	0.1	0.2912	3.5	0.3	4.91	100.4	109.4
	12	9.7	9.6		190.3	10.0	0.3	0.1340	7.0	0.3	4.25	91.0	109.7
	10	6.3	6.3		97.3	6.4	0	0.0857	1.8	. . .	3.93	88.9	95.1
484.2	10	7.7	. . .	8.414	58.0	16.1	0.6	0.3115	20.9	1.1	5.01	116.4	133.2
	13	3.6	. . .		123.3	7.8	0.6	0.3123	6.7	1.2	3.80	130.6	135.9
(2.75)	10	3.7	. . .		99.5	13.1	0.2	0.2307	4.7	1.7	4.77	128.9	149.5
	10	5.9	. . .		34.3	17.6	0.1	0.2813	4.7	1.2	5.47	121.0	143.7
	5	6.3	. . .		63.6	11.9	0.1	0.1387	5.0	1.7	5.21	123.4	149.4
507.6 p	8	3.9	3.4	20.19	196.3	11.8	0.9	0.8065	6.1	~0	4.42	183.7	187.6
p	5	13.5	12.4		69.7	22	1.3	0.9970	5.1	~0	5.00	191.4	192.5
(2.62)p	6	2.3	2.3		45.3	14.7	0.3	0.5095	3.3	~0	4.66	224.3	236.2
p	9	3.7	3.7		118.2	6.7	0.9	1.0370	3.3	~0	3.78	203.5	204.0
514.4	5	4.4	4.0	25.70	53.0	12.0	0.2	0.8490	1.4	0.7	4.20	233.0	235.4
	5	1.9	1.9		68.5	6.2	0.1	0.5520	2.3	0.7	3.29	245.6	248.0
(2.58)	5	3.3	2.7		118.7	8.5	0.6	0.7275	3.1	0.5	3.56	241.3	244.1
	4	6.6	5.7		63.2	12.3	0.3	0.8905	2.3	0.6	3.68	250.8	252.8
	8	2.1	2.1		93.3	9.3	0.6	1.0130	3.4	0.6	3.23	235.5	235.7

[a] p = packed vessel, no marks = unpacked vessel. The values in parenthesis are equilibrium data obtained previously for the geometrical isomers of $PD_{1,3}$ (compare with column 12). [b] $[I_2]_0$ and $[I_2]_f$ stand for initial and final iodine pressure, respectively. [c] $K_{I_2}{}^{1/2}$ is the equilibrium constant for the dissociation of $I_2 \rightleftarrows 2I$. [d] $[PD_{1,4}]$ and $[PD_{1,4}]_f$ stand for initial and final 1,4-pentadiene. [e] Based on pressure–volume–temperature measurements. [f] Over-all pressure loss. [g] Based on analysis by gas chromatography (*cf.* eq. 4 in text). $[PD_{1,3}]$ stands for 1,3 pentadiene; *t* and *c* for the *cis* and *trans* isomer, respectively. P_2 denotes 2-pentene, P_c cyclopentene. [h] The formation of higher boiling hydrocarbons (dimers), calculated from the material balance, is included in the conversion. [i] Not used to compute Arrhenius parameters.

1-pentene, 12.9; 1,4-pentadiene, 13.0; isoprene, 19.1; *trans*-1,3-pentadiene, 23.7; *cis*-1,3-pentadiene, 27.5; cyclopentane, cyclopentene, and cyclopentadiene, 31.6; *n*-hexane, 36.0; and 1-methyl-1-cyclopentene, 80.3.

The reaction products of a few selected runs have in addition been analyzed, using a 12-ft. column of BMEA[6] operated at room temperature. This column resolved the cyclic C_5 hydrocarbons and separated *n*-pentane from 1,4-pentadiene. The cyclic product was identified as exclusively cyclopentene, and no significant amounts of *n*-pentane were found to be present. The above column of silicone oil therefore was suitable for our purposes and was chosen over BMEA, because of the complete separation of the 2-pentenes from 1,4-pentadiene. 1-Pentene, however, is completely overlapped by 1,4-pentadiene. As was expected, *n*-pentenes were found to be present in their equilibrium concentrations,[7] and usually only in rather small amounts (compare Table I, column 11). The amount of 1-pentene present is therefore trivial, as the equilibrium constant $K_{3,4}$ between *trans*-2-pentene and 1-pentene is between 6 and 11 over the temperature range used. A disk chart integrator gave peak areas. The reproducibility of the analysis shown in Table I was found to be within ±2% (maximum deviation).

Results

For the iodine catalyzed isomerization of 1,4-pentadiene ($PD_{1,4}$) we can write

$$I + PD_{1,4} \underset{k_2}{\overset{k_1}{\rightleftarrows}} PD_{1,3} + I \qquad (1)$$

and the rate expression for the disappearance of 1,4-pentadiene with time is

$$\frac{-d(PD_{1,4})}{dt} = k_1(PD_{1,4})(I) - k_2(PD_{1,3})(I) \qquad (2)$$

For all practical purposes and up to very high conversions, the back reaction k_2 can be neglected as the equilibrium of reaction 1 is way over on the side of the conjugated diene, which is stabilized by more than 5 kcal./mole.[8] Equation 2 therefore reduces to the very

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[7] K. W. Egger and S. W. Benson, *J. Am. Chem. Soc.*, **88**, 236 (1966).

[8] Standard heats of formation taken from "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons," American Petroleum Institute, Carnegie Press, Pittsburgh, Pa., 1953.

simple first term and yields upon integration

$$k_1 = \frac{-2.303}{(\mathrm{I})t}\log\left\{\frac{[\mathrm{PD}_{1,4}]_f}{[\mathrm{PD}_{1,4}]_0}\right\}$$

Upon setting $(\mathrm{I}) = K_{\mathrm{I}_2}{}^{1/2}(\mathrm{I}_2)$, where K_{I_2} is the equilibrium constant for the dissociation of I_2,[9] and using the stoichiometric relation that the initial concentration of 1,4-pentadiene ($[\mathrm{PD}_{1,4}]_0$) equals the total amount of 1,4-pentadiene ($[\mathrm{PD}_{1,4}]_f$) and 1,3-pentadiene ($[\mathrm{DP}_{1,3}]$) at the end of the reaction in the absence of side reactions

$$k_1 = -\frac{2.303}{K_{\mathrm{I}_2}{}^{1/2}(\mathrm{I}_2)^{1/2}t}\log\left\{\frac{1}{1 + [\mathrm{PD}_{1,3}/\mathrm{PD}_{1,4}]_f}\right\} \quad (3)$$

However, as part of the reaction products *n*-pentenes (P_n) and cyclopentene (P_c) have been found besides the main products *trans*- and *cis*-1,3-pentadiene. The results of the measured product distribution are shown in columns 8, 9, and 10 of Table I. P_n and P_c comprise in most of the experiments between 5 and 10% of the 1,3-pentadiene formed and only at the two lowest temperatures do they make up to 30% of the $\mathrm{PD}_{1,3}$. Both *n*-pentenes and cyclopentene have to be included in the over-all conversion. As shown in the discussion section of this paper, the reaction proceeds through the initial abstraction of a hydrogen atom from $\mathrm{PD}_{1,4}$, forming HI and pentadienyl radicals as intermediates. *n*-Pentenes result from HI adding to 1,3-pentadiene,[10] and cyclopentene is a product of the alternate cyclization route of the pentadienyl radical. Equation 3 can therefore be written as

$$k_1 = -\frac{2.303}{K_{\mathrm{I}_2}{}^{1/2}(\mathrm{I}_2)^{1/2}t}\log\left\{\frac{1}{1 + [(\mathrm{PD}_{1,3} + \mathrm{P}_n + \mathrm{P}_c)/\mathrm{PD}_{1,4}]_f}\right\} \quad (4)$$

Table I contains in the second to last column values for the rate constant k_1 obtained from eq. 4, and Figure 1 shows an Arrhenius plot of the same data in units of mm.$^{-1}$ min.$^{-1}$. A regular least-squares fit regression program on a Burroughs 5500 computer was used to get the best fit of our data to a straight line. Disregarding the unreliable measurements at the lowest temperature (402°K.) and not taking into account the packed vessel points at 429.3°K. we obtain with standard errors

$$\log k_1\,(\mathrm{l./mole\ sec.}) = (9.15 \pm 0.11) - (9.60 \pm 0.25)/\theta$$

$$\theta = 2.303RT\,(\mathrm{kcal./mole})$$

The multiple correlation coefficient, a measure of the accuracy of the fit of our data to the computed linear equation, is 0.9901, compared to 1.0000 for an ideal fit. This result shows that the form of the rate expression is satisfied with very consistent k_1 values at any given temperature. Up to sixfold variation in hydrocarbon and initial iodine pressures have been used and the ratio of hydrocarbon to iodine pressure covers a very wide range between 1.8 and 45. Up to 340 torr of 1,4-pentadiene have been used, and conversions between ~4 and ~50% have been realized.

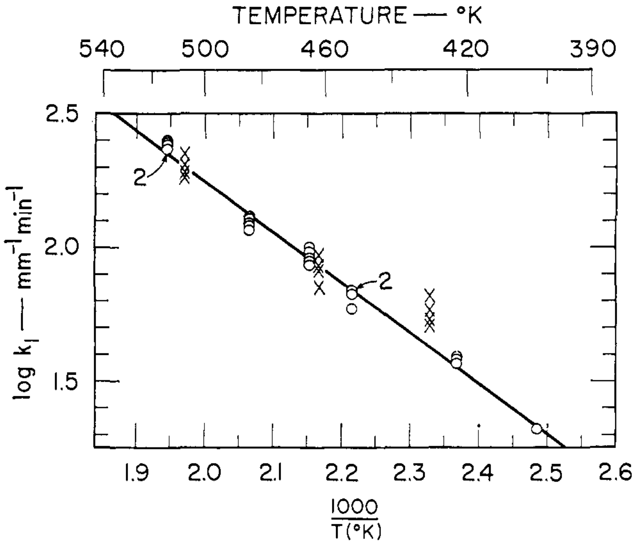

Figure 1. Arrhenius plot of the rate constant for the positional isomerization of 1,4-pentadiene. The crosses represent data obtained using a packed reaction vessel; numbers indicate overlapping points.

The isomerization of 1,4-pentadiene as well as the addition of HI to 1,3-pentadiene and the dimerization reaction of the dienes proved to be very surface sensitive. Only with Teflon-coated reaction vessels have we been successful in eliminating the heterogeneous reactions on the glass walls. As can be seen from Table I and Figure 1, the rate constants do not change when the packed reaction vessel, with an 18-fold larger surface to volume ratio than the nonpacked vessel, is used. A small contribution from surface reactions can be seen from the results at the lowest temperature of 429°K. in the packed reaction vessel. The measured rate constant of 59.1 is a factor of 1.4 higher than the homogeneous rate constant at this temperature. This is considered a small change and is only measurable at the very low temperatures.

The values of k_1 reported in Table I, disregarding the unreliable low-temperature points at 402°K., show maximum deviations from the mean value of up to 8% using the nonpacked vessel and about twice as much using the packed vessel. The expected scatter from all experimental sources alone is about ±5%. Part of the scatter is to be expected as arising from the measured differences in the material balance of the various runs (compare column 7, Table I).

The defect in material balance seems to be of a random nature, and no trend or dependence on any of the known and controllable experimental parameters has been detected. The fact that the loss in material appears to be independent of the conversion and temperature of a particular run indicates that the material not accounted for was not formed by the intermediate pentadienyl radical or any secondary reactions of primary reaction products. The most likely reaction that would lead to a loss in C_5 hydrocarbons is the dimerization between the pentadienyl radical and/or 1,3-pentadiene with 1,4-pentadiene. This reaction would however have resulted in a pressure loss during the reaction. No significant pressure changes have been measurable in all of our experiments (compare column 8 in Table I).

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[9] "JANAF Interim Thermochemical Tables," Dow Chemical Co., Midland, Mich., 1960.

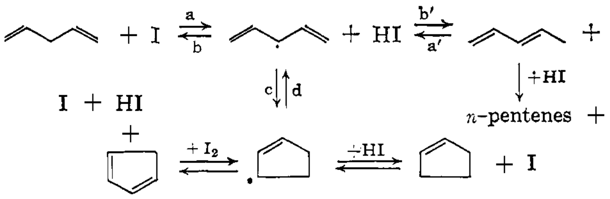
[10] K. W. Egger and S. W. Benson, *J. Am. Chem. Soc.*, in press.

A compensation of a pressure loss by some other side reaction yielding a pressure increase can be excluded, as such a reaction would have to have the same rate as the dimerization over the complete temperature range studied. The most reasonable explanation for the measured material unbalance is a loss during the collection of the sample. Any material that has a vapor pressure of a few torr or less at −15° would be condensed together with the iodine and escape our measurement. Indeed, we find liquid condensates in the iodine trap. A possible explanation would be that we are forming iodides upon cooling our reaction mixtures, which then are collected in the two first traps, held at −15°. There are no iodides formed in the reaction vessel except at the low temperatures around 400°K. where one necessarily has to use large amounts of iodine. The increased stability of iodides is considered to be the main reason for the large scatter of our results at these temperatures which makes these values unreliable. To get an idea about the errors introduced into k_1 if the loss in material balance were actually caused by a loss of conversion products, corrected rate constants $(k_1)^{\text{cor}}$ have been calculated. The results are shown in the last column of Table I. As can be seen, the correction does not alter the k_1 values too much. In most cases k_1^{cor} is about 5 to 10% larger than k_1, and only at the lowest temperatures do we see large changes in k_1 of up to 50% and more. In addition the k_1^{cor} data do not fit a linear equation nearly as well as the incorrected k_1 data. Our data are therefore used without applying any corrections.

Altering the collection procedure had no effect on the material balance. There is another interesting feature about the product distribution that deserves to be mentioned in this connection. It was quite surprising that *trans*- and *cis*-1,3-pentadiene were not formed, or at least did not show up in the analysis at their equilibrium concentrations. This will be discussed in the next section. The most reasonable explanation seems to be that we preferentially lose some of the *cis* isomer during the quenching and sampling of the reaction products. The measured ratio of the geometrical isomers is given in Table I in column 12, "product distribution," and the equilibrium ratio of $PD_{1,3}$ *trans*/*cis* as has been reported earlier[11] is shown in parentheses in the column listing the reaction temperatures.

Discussion

The mechanism for the radical-catalyzed positional isomerization of olefins has previously been discussed for the case of the isomerization of the *n*-butenes. In the present case it involves abstraction of a hydrogen atom from a secondary carbon bonded to two vinyl groups in 1,4-pentadiene. A complete over-all detailed reaction scheme, including all anticipated reaction steps, is given below.



(5)

(a) Stabilization Energy. As has been expected, the hydrogen abstraction from 1,4-pentadiene to form the intermediate pentadienyl radical is the rate-controlling step in the system. This is confirmed by the consistent k_1 values obtained in this work (compare eq. 1). In accordance with the results on the isomerization of 1-butene, it can be assumed that the ratio of k_b/k_b' is very close to unity and nearly temperature independent. The observed over-all rate constant k_1 therefore equals $^1/_2k_a$. For all practical considerations, k_a', and hence k_2, can be neglected, as the activation energy E_a is about 6 kcal. lower than E_a' (conjugation energies plus the difference between primary and secondary bond strength). The pentadienyl radical intermediate is stiffened and stabilized by the distribution of the available "extra" five electrons compared to the bonding electrons of a simple C–C bond. For *n*-butenyl radical with only three "extra" electrons, this stabilization energy, also called allylic resonance, has been reported previously[2a] to be 12.6 ± 1.0 kcal./mole. This work yields the activation energy $E_1 = 9.6 \pm 0.3$ kcal./mole for the hydrogen abstraction from a carbon atom bonded to two vinyl groups. Let us define a "dienyl" stabilization energy as the difference in dissociation energies at a given temperature (D^T) between a C–H bond conjugated to two double bonds and the corresponding C–H bond in the parent saturated hydrocarbon.

$$\text{"dienyl" stabilization energy} = D^T(\text{secondary C–H})_{n\text{-pentane}} - D^T(\text{secondary C–H})_{n\text{-pentadiene-1,4}} \quad (6)$$

Nangia and Benson[12c] studied the kinetics of the iodine catalyzed abstraction of a secondary hydrogen atom from propane. For the activation energy of that process, they obtained in analogy to E_1 $E_1' = 25 \pm 0.5$ kcal./mole. It can be assumed that the activation energy for the hydrogen abstraction from *n*-pentane by iodine atoms (E_1'') is not more than about 0.5 kcal. different from the above value for *n*-propane. We take $E_1' = E_1'' = 25 \pm 0.5$ kcal./mole.

The stabilization energy, defined in eq. 6, is given by the differences in the activation energies $(E' - E_1)$ for the hydrogen abstraction from *n*-pentane and *n*-pentadiene reduced by the difference in the activation energies of their back reactions $[E_b' - E_b]$. The rate constants for the back reaction, the HI attack on a secondary pentadienyl (E_b) and on pentyl radical (E_b'), are not expected to be very different. Based on the reported differences[12a-d] in activation energies between the values for ethyl and acetyl radical reacting with HI, one can assume $E_b' - E_b$ to be 0 ± 0.5 kcal.

$$\begin{aligned}\text{"dienyl" stabilization energy} &= [(E_1' - E_1)] - [(E_b' - E_b)] \\ &= [(E_1' - E_1)] - [0 \pm 0.5] \\ &= (25.0 \pm 0.5) - (9.60 \pm 0.25) - (0 \pm 0.5) \\ &= 15.4 \pm 0.75\end{aligned}$$

If the error limits are broadened to take any possible

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[11] K. W. Egger and S. W. Benson, *J. Am. Chem. Soc.*, **87**, 3311 (1965).

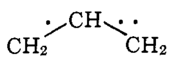
[12] (a) M. C. Flowers and S. W. Benson, *J. Chem. Phys.*, **38**, 882 (1963); (b) D. B. Hartley and S. W. Benson, *ibid.*, **39**, 132 (1963); (c) P. Nangia and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 2773 (1964); (d) H. E. O'Neal and S. W. Benson, *J. Chem. Phys.*, **37**, 540 (1962).

differences for the secondary C–H bond in *n*-propane and *n*-pentane into account, we can write for the stabilization energy in the pentadienyl radical 15.4 ± 1.0 kcal./mole. This value is to be considered a lower limit since the assumptions that $k_b = k_b'$ and $E' = E''$, while generally reasonable, have not been proven for the pentadienyl radical.

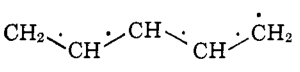
At present a fair amount of information about the magnitude of stabilization or "resonance" energies in linear and cyclic compounds is available to allow from a quantitative point of view the following tentative interpretation of the nature and source of this stabilization energy. The known, directly measured stabilization energies, defined as discussed earlier in this work, are 12.6 kcal. for noncyclic allyl radicals and 15.5 for dienyl radicals. Benzene is stabilized by 36 kcal. Recent studies in this laboratory[13] and the reported rate constants for the addition of CH_3[14a] and CF_3[14b] radicals to benzene strongly support a stabilization energy in the cyclohexadienyl radicals of about 23 to 25 kcal., or about twice that in linear allyl radicals and two-thirds that of benzene.

One of the original reasons for proposing resonance in benzene was the adherence to a bonding model in which only single and double bonds were permitted.[15] If, however, one relaxes such arbitrary restrictions and permits one- and three-electron bonds, then the ground state of benzene is very simply and also much more quantitatively[16] described by six equivalent bonds containing two σ electrons and one π electron. Then quite ironically there is no resonance in the ground state of benzene. Such a model is on electrostatic grounds very reasonable since the total number of bonding electrons remains the same, but electron–electron repulsions are reduced.

From this point of view, the allyl radical π bonding may thus be pictured as A while the pentadienyl radical π-bonding would be B. In both cases we have semi-ion pair structures at the terminal C atoms, which are internally compensated by symmetry and also undoubtedly by polarization. From a purely empirical point of view, it may be deduced from the allyl stabilization energy of 12.6 kcal. that the replacement of a double and a single bond by two three-electron bonds is exothermic by this same 12.6 kcal. It then seems quite reasonable that the benzene stabilization energy should be about three times this value, and in fact the observed value of 36 kcal. fits such a picture quite well.[17]



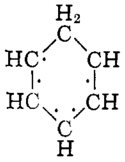
A



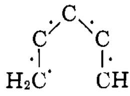
B

Since structures A and B are written with formal charges of +½ on the extreme left-hand CH_2 groups and −½ on the extreme right-hand CH_2 groups, they have been labeled semi-ion pairs.[18] They have symmetrical, equivalent "resonance" forms in which the charge distribution is reversed.

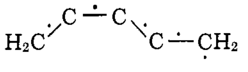
Interpolating such a theory to pentadienyl, one might anticipate a stabilization energy of about twice that of the allyl or about 24 kcal. In contrast we observe about 16 kcal. As mentioned before, considerable evidence exists that in the cyclohexadienyl radical the stabilization energy is very close to 24 kcal., thus indicating an extra stability for the more compact ring structure of about 7–8 kcal. While we have no quantitative explanation of such an extra stabilization, it does seem reasonable in terms of the formal charges required by the semi-ion pairs of structures A and B. In the cyclohexadienyl radical (C), the formal charges are separated by about the same distance as in the allyl radical. Hence it is electrostatically a more stable system than the open-chain pentadienyl (B). One might then expect that, if this is the case, pentadienyl radicals should prefer a more compact *cis–cis* structure (B′) or *cis–trans* structure (B″). There is however a considerable steric cost in converting B into B′ or B″, which might well outweigh the electrostatic gain.



C



B′



B″

Bates, *et al.*,[19] reported that U-shaped pentadienyl carbanions are more stable by 2–5 kcal. than *cis–trans* or *trans–trans* configurations of the same ion. Even though the pentadienyl radical and anion are not directly comparable, one might expect very similar relative stabilities of their different conformational forms. Studies are under way to obtain more quantitative information on differences in stabilization energies of cyclic and open-chain compounds.

(b) Dimerization. The pentadienyl radical intermediate can react with HI or add to 1,4-pentadiene to form dimeric products before abstracting a hydrogen from HI. The fact that we see no pressure losses shows the the addition reaction is not an important route for the radical at these temperatures. This finding is consistent with the thermal dimerization rate reported by Harkness, *et al.*,[4] for 1,3-pentadiene and from independent studies of our own.[20]

(c) Cyclization. The fact that we find small amounts of cyclic reaction products shows that some of the pentadienyl radicals can undergo cyclization before they are attacked by HI.

The equilibrium between the open-chain and the cyclic form of the radical can be estimated as follows. The cyclization reaction is about 14 kcal. exothermic

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(13) K. W. Egger and S. W. Benson, unpublished work.

(14) (a) M. Levy and M. Szwarc, *J. Am. Chem. Soc.*, 77, 1949 (1955); (b) J. R. Major, D. Phillips, and J. C. Robb, *Trans. Faraday Soc.*, 61, 110 (1965).

(15) See particularly the discussion in G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 6.

(16) P. B. Empedocles and J. W. Linnett, *Proc. Roy. Soc.* (London), **A282**, 166 (1964); see also J. W. Linnett, "The Electronic Structure of Molecules: A New Approach," John Wiley and Sons, Inc., New York, N. Y., 1964.

(17) S. W. Benson, *J. Chem. Educ.*, 42, 502 (1965).

(18) S. W. Benson, *Advan. Photochem.*, **2**, 1 (1964); S. W. Benson and A. N. Bose, *J. Chem. Phys.*, **39**, 3463 (1963).

(19) R. B. Bates, R. H. Carnighan, and C. E. Staples, *J. Am. Chem. Soc.*, **85**, 3031 (1963).

(20) K. W. Egger and S. W. Benson, to be submitted.

(formation of a C–C bond in the cyclopentenyl radical of ~81 kcal. and loss of a double bond of ~57 kcal., taking into account 7 kcal. in strain energy in the ring and a loss of 15.4 − 12.6 = 2.8 kcal. in stabilization energy in going to the cyclic product). The entropy difference between the two radical intermediates is not expected to exceed 5 to 7 e.u. The A factor for ring opening (A_d) can be estimated to 10^{13} in accordance with most other reactions involving unimolecular bond breaking. The A factor for ring closure (A_c) is therefore about $\sim 10^{12}$. The equilibrium between the linear and cyclic radicals is way over on the side of the cyclopentenyl radical. The fact that only small amounts of cyclic products are formed must mean that the cyclization reaction requires a high activation energy. The magnitude of this activation energy E_c can be estimated from the relative rates of ring closure *vs.* HI attack on the pentadienyl radical. The product analysis shows that not more than ~1% of the total reaction products were found to be cyclopentene. This means that the rate of HI attack on the pentadienyl radical (k_b) is about 100 times faster than the rate of ring closure (k_c) to form the isomeric cyclopentenyl radical.

$$\frac{k_b'(\mathrm{HI})}{k_c} \approx 100 \approx \frac{(10^{8\pm1})(10^{-1.5\ \pm\ 0.5/\theta})(10^{-5})}{10^{12}10^{-E_c/\theta}}$$

Previous experiences with HI attack on radicals[12a–d] yield the above value of k_b' (units of l. mole^{-1} sec.$^{-1}$).

From the fact that we lose practically no iodine during the course of the reaction and from the sensitivity of the iodine measurements, one may assume that (HI) $\lesssim$ 0.5 torr. For A_c we use the value of 10^{12} mentioned earlier. For a mean temperature of 450°K. this yields 24 kcal. for E_c', the activation energy for ring closure. This value seems to be reasonable. Together with the estimated exothermicity of 14 kcal., it leads to a value of about 38 kcal. for the activation energy of the reverse reaction, ring opening of cyclopentenyl to form the pentadienyl radical. This can be compared with the recently reported values of 37 kcal. for the similar ring opening of cyclopentyl radical to form 1-penten-5-yl radical.[21] This latter reaction is endothermic by about 17 kcal.

(d) Rotation in the Pentadienyl Radical. Conformational changes in the radical intermediate are expected to be reasonably fast. The barrier to rotation can be estimated to be not more than 6–7 kcal. Only about 3 kcal. of stabilization energy are given up in forming the pentenyl radical, which should have a barrier to rotation of about 3 kcal. (judging from similar molecules).[22] This then means that the 1,3-pentadiene formed should be in equilibrium with respect to the geometrical isomers. In addition we know from earlier measurements of the kinetics[5a] and the equilibrium[11] between *cis* and *trans* $\mathrm{PD}_{1,3}$ that the iodine catalyzed geometrical isomerization of 1,3-pentadiene is very fast at the temperatures and iodine concentrations used in this work. Yet we do not find the geometrical isomers of $\mathrm{PD}_{1,3}$ in equilibrium concentrations. We believe that this arises from small stereospecific losses while quenching and collecting the sample. This conclusion is supported by the reported material defects.

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(21) A. S. Gordon, *Can. J. Chem.*, **43**, 570 (1965); H. E. Gunning and R. L. Stock, *ibid.*, **42**, 357 (1964).

(22) H. G. Silver and T. L. Wood, *Trans. Faraday Soc.*, **59**, 588 (1963).

Determination of the Dissociation Rate of Dodecylpyridinium Iodide Micelles by a Temperature-Jump Technique[1a,b]

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Abstract: The rate of dissociation of the dodecylpyridinium iodide micelle in aqueous solution was studied by a temperature-jump technique in order to investigate the kinetic aspects of micellization. A relaxation process with a concentration-dependent half-life was observed above the critical micelle concentration. The temperature dependence of the rate constant k, which corresponds to dissociation of the first monomer from the micelle, can be described by the equation $\ln k = -1750/RT + 6.91$ over the range 8–22°. A mechanism has been proposed which is consistent with the characteristics of micellization, and possibly involving an activation process in which water is ordered around a monomer as it leaves the micelle. The techniques applied in this investigation should be applicable in general for studies of the association of macromolecules.

Although numerous studies have been made to elucidate the equilibrium aspects of micellization, the kinetics of micellization have been neglected. This is probably due to the fact that the rate of micellization is so fast that it cannot be followed by conventional techniques.[3–5]

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(2) (a) National Institutes of Health Postdoctoral Fellow of the National Cancer Institute, 1963–1965; (b) National Institutes of Health Postdoctoral Fellow of the National Institute of General Medical Sciences, 1964–1966.

(3) G. S. Hartley, *Trans. Faraday Soc.*, 31, 199 (1935).

(4) G. A. Phillips and A. S. Porter, *Vortraege Originalfassung Intern. Kongr. Grenzflaechenaktive Stoffe, 3, Cologne, Germany*, 1, 239 (1960) (published 1961); *Chem. Abstr.*, 57, 6049*f* (1962).

(5) P. Mukerjee and K. J. Mysels, *J. Am. Chem. Soc.*, 77, 2937 (1955).