126. *The Mechanism of Additions to Double Bonds. Part XIV.* The Nature of the Activated Complex in Bimolecular Diene Syntheses.*

By Albert Wassermann.

The rate-determining step in the bimolecular dimerisation of gaseous butadiene might involve an activated complex stereochemically similar to (*a*) 4-vinyl*cyclo*hexene or (*b*) an open-chain diradical which is subsequently converted into the cyclic product. In discussing these two possibilities, Kistiakowsky and Ransom concluded that mechanism (*b*) is operative, but it is now shown that this mode of addition is not proved. Attention is directed to the fact that the kinetic course of the association of butadiene and of other bimolecular diene syntheses is not altered by oxygen or peroxides, and this indicates that free radicals do not play a rôle as intermediates. It appears more probable, therefore, that the slowest stage of these processes involves activated complexes of the same stereochemical type as the stable product molecules.

An attempt is here made to find out whether bimolecular diene syntheses (Diels–Alder reactions) involve activated complexes which are stereochemically similar to the product, or whether the rate-determining step consists in the formation of radicals which are subsequently converted into the stable associated species. The first mode of addition is characterised by bimolecular collisions in which a close contact between the carbon atoms of the reactants occurs at two specified positions, whereas the slowest stage of the alternative mechanism is of such a nature that a close contact between the carbon atoms of the reactants occurs at one point only. In order to decide between these possibilities Kistiakowsky and Ransom (*J. Chem. Physics*, 1939, **7**, 725)

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* For Parts XI—XIII, see *Trans. Faraday Soc.*, 1939, **35**, 841, 1022; J., 1940, 735.

attempted to estimate the entropy of activation of the simplest gaseous diene synthesis, *viz.*, the dimerisation of butadiene :

Butadiene. 4-Vinyl*cyclo*hexene.

$$. . . . . . (1)$$
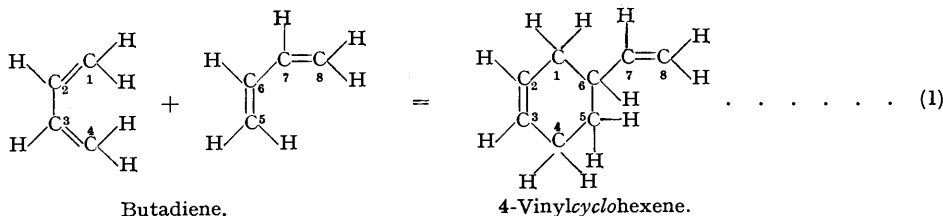
The *a priori* calculation was made on the assumption that the activated complex is stereochemically similar either to (*a*) 4-vinyl*cyclo*hexene or to (*b*) the open-chain diradical (I), and a comparison of the theoretical

(I.)
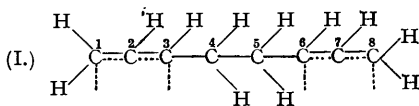
(The bonds between atoms 1, 2, and 3, and 6, 7, and 8 are assumed to be intermediate between ordinary double and single bonds. The four vertical dotted lines indicate two free valencies. Formation of a bond between the carbon atoms 1 and 6 leads to 4-vinyl*cyclo*hexene.)

values with the experimental entropy of activation seemed to indicate that mechanism (*b*) is operative. It will now be shown that this mode of addition is not proved, and that a number of observations provide arguments against the supposition that in the dimerisation of butadiene or in kinetically similar diene syntheses the transient formation of free radicals takes place. It should be noted, however, that the following considerations relate to thermal Diels–Alder reactions which have been the subject of a kinetic investigation and that it is not within the scope of this paper to deal with those additions to substituted styrenes which, according to Hudson and Robinson (J., 1941, 715), are initiated by the part formation of one co-ordinated link between the associating molecules. It is also not intended to discuss diene reactions which occur as a result of photochemical or catalytic processes or which depend on the migration of hydrogen atoms.

The Entropy of Activation in the Dimerisation of Butadiene.—The bimolecular velocity coefficient of the dimerisation of gaseous butadiene can be represented (cf. Glasstone, Laidler, and Eyring, " Theory of Rate Processes," New York, 1941, p. 198) by

$$\text{velocity coefficient} = A e^{-E/RT} = \kappa (kT/h) e^2 e^{\Delta S*/R} e^{-E/RT} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where E is the Arrhenius activation energy and κ the transmission coefficient. An approximate estimate of the entropy of activation, $\Delta S*$, can be made by using the standard formulæ in Table I (see Fowler and

TABLE I.

Standard Formulæ for Entropy Calculations.

Freedom.	Contribution to S/R and to $S*/R$.
Translation (relating to g.-mol. and cm.³)	$1 \cdot 299 + \log_e \left\{ \left(\frac{T}{100 \text{ deg.}} \right)^{3/2} M^{3/2} \right\}$
External rotation	$3 \cdot 46 + \log_e \left\{ \frac{(I'I''I''')^{1/2}}{(10^{-40} \text{ g.-cm.}^2)^{3/2}} \left(\frac{T}{100 \text{ deg.}} \right)^{3/2} \frac{1}{\sigma} \right\}$
Harmonic vibration	$\frac{\Theta/T}{e^{\Theta/T} - 1} + \log_e \{ (1 - e^{-\Theta/T})^{-1} \}$
Internal rotation	$1 \cdot 54 + \log_e \left\{ \left(\frac{i}{10^{-40} \text{ g.-cm.}^2} \right)^{1/2} \left(\frac{T}{100 \text{ deg.}} \right)^{1/2} \frac{1}{\sigma_i} \right\}$

Guggenheim, " Statistical Thermodynamics," Cambridge, 1939), in which the symbols have the following meanings : M is the molecular weight on the conventional chemical scale, I', I'', I''' are the principal moments of inertia, σ is the external symmetry number, Θ is the frequency of a harmonic internal vibration expressed in terms of temperature by using the relation $h\nu = kT$, i is the reduced moment of inertia, and σ_i is the symmetry number appropriate to the internal rotations. In applying some of these formulæ it has to be borne in mind that butadiene and the two types of activated complex are resonance hybrids, so that in principle the entropy should be computed for a number of different contributing structures. The calculations in this communication relate, however, to one set of bond assignments only. These are as follows. *Butadiene :* the ordinary formula is employed. *Cyclic activated complex :* the two carbon–carbon bonds between the atoms 1, 6 and 4, 5 are not fully formed (cf. below) but otherwise the bond assignment is regarded as identical with that in 4-vinyl*cyclo*hexene. *Open-chain activated complex :* the species here considered is assumed to be identical with (I), except in so far as the carbon–carbon bond between atoms 4 and 5 is not fully formed. Kistiakowsky and Ransom assumed that (I) consists both of a triplet, and a singlet state of nearly equal energy, whereas butadiene is, of course, in a singlet state. The supposed change of electron multiplicity was taken care of by a term $R \ln 4$, which was added to the other entropy contributions. This procedure has not been adopted, for it is not clear how a singlet state can change with sufficient speed, in the absence of a magnetic field, into a triplet state. It should be noted, however, that the coupling between the spins of the electrons designated by

the four dotted vertical lines in (I) will be so loose that species (I) can at any rate be described as a " diradical " even if a triplet state is not formed, and that the term $R \ln 4$ is numerically smaller than the inaccuracies of the rotational and vibrational entropy contributions, so that it is irrelevant for all the following conclusions whether it is included in the total entropy change or whether it is omitted. The possible formation of a branched-chain isomer of (I) has been disregarded by Kistiakowsky and Ransom and, therefore, it is not necessary to estimate the entropy of this stereochemically different radical.

The lengths of the C—C, C⁝⁝⁝C, and C⚌C bonds in all the above species have been assumed to be respectively 1·5, 1·4, and 1·35 A. It is realised that the bond lengths of ordinary molecules and activated complexes cannot exactly agree, but the difference can be neglected for the purpose of the present approximate entropy calculations, which relate moreover to species the stereochemical configuration of which is unknown.

TABLE II.

Data for Calculation of Contributions due to Translation and External Rotation.

| | | Butadiene. | Activated complex. | |
			Cyclic.	Open-chain.
M		54·1	108	108
$(I'I''I''')^{1/2} \frac{10^{58}}{3/2\text{-cm.}^3}$ ⎰Maximum		10	98	110
⎱Minimum		6	78	10
⎱Mean		8	88	60
σ		2	1	2

The principal moments of inertia in Table II, which are required for the estimation of the various contributions due to the external rotations, are the roots of the secular equation (3), where m is the mass of the CH

$$\begin{vmatrix} \Sigma m(\text{y}^2 + z^2) - I & \Sigma mxy & \Sigma mxz \\ \Sigma myx & \Sigma m(z^2 + x^2) - I & \Sigma myz \\ \Sigma mxz & \Sigma myz & \Sigma m(x^2 + y^2) - I \end{vmatrix} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and CH$_2$ group and x, y, and z are their rectangular co-ordinates referred to the centre of gravity of the molecule and with arbitrary directions. The reactants and the activated complexes were represented by models of steel wire in which the hydrogen atoms coincided with adjacent carbon atoms (cf. Kistiakowsky and Ransom) and the bond angles were between the tetrahedral angle and 120°. The models were so large that the co-ordinates of the various CH and CH$_2$ groups could be estimated by carrying out measurements with a ruler, the distances so obtained being 10^9 times larger than the relevant x, y, or z values of equation (3). The maximum and minimum moments of inertia in Table II refer in the case of butadiene to the plane *cis*- and *trans*-form, and in the case of the cyclic activated complex to configurations which are distinguished by the position of the extracyclic vinyl group. The maximum moments of inertia of the open-chain activated complex relate to an extended zigzag form which is similar to the grouping of the middle part of the diphenyloctatetraene molecule in the solid state (Kuhn and Hengstenberg, *Z. Krist.*, 1930, **75**, 301), while the minimum moments of inertia refer to a closely packed configuration in which the CH and CH$_2$ groups are in the corners of a distorted cube.

The contributions due to harmonic vibrations and internal rotations were estimated by using Pitzer's rules (*J. Chem. Physics*, 1937, **5**, 469, 473) and the formulæ in lines 3 and 4 of Table I. The vibrational and rotational classes, the number of modes, and the assumed frequencies are listed in Table III, which for reasons given below is divided into two parts α and β. The data relate to two butadiene molecules, to the cyclic and the open-chain activated complex, and, for the sake of comparison, reference is also made to the relevant fully formed associated species. The difference between the latter molecules and the activated complexes is assumed to consist in the number of those carbon–carbon stretching and bending modes which are listed in lines 5 and 9 of Table III. It should be noted that the cyclic and the open-chain activated complex have only respectively four and two C—C stretching modes. This is due to the fact that the normal vibrational frequency in the co-ordinate of reaction has an imaginary value.

All the vibrational frequencies except the one indicated by an asterisk were taken from Kistiakowsky and Ransom, who computed the vibrational entropy of butadiene and of the open-chain activated complex by using Pitzer's method. For the cyclic species, however, they estimated the total entropy with the help of thermochemical data and of an empirical rule for the calculation of heat capacities. The present computation of the entropy of the cyclic activated complex has been carried out by using the same method as that employed for the other species and involves the assumption that the frequencies of all the carbon–carbon bending modes are equal to each other and are as low as 190 cm.$^{-1}$. Although in benzene or simple aromatic compounds such low frequencies do not occur (cf., *e.g.*, Lord, Ahlberg, and Andrews, *J. Chem. Physics*, 1937, **5**, 649), it is nevertheless believed that the above estimate is not unreasonable, for data have been presented (Wassermann, *Proc. Roy. Soc.*, 1941, *A*, **178**, 370) which are consistent with the assumption that in certain derivatives of *cyclo*hexene some of the vibrational frequencies are as low as 190 cm.$^{-1}$ or even lower. Kistiakowsky and Ransom referred to a cyclic activated complex stereochemically similar to 4-vinyl*cyclo*hexene with " a half dozen frequencies of 150 cm.$^{-1}$ " and pointed out that this assignment would bring theory and experiment together, but in contrast with the present point of view they regarded the assumption of low frequencies as so improbable that the stepwise mechanism of the formation and decomposition of 4-vinyl*cyclo*hexene was believed to be proved.

TABLE III.

Data for Calculation of Contributions due to Vibrations and Internal Rotations.

Number of vibrations or internal rotations.

Vibrational class (including internal rotations).	2 Butadiene.	Activated complex. Cyclic.	Activated complex. Open-chain.	Fully-formed associated species. Cyclic.	Fully-formed associated species. Open-chain.	Frequency (cm.$^{-1}$).
α 1. C—H stretching	12	12	12	12	12	3000
2. $\frac{H}{H}$>C bending	4	4	4	4	4	1440
3. H—C—C, H—C=C, or H—C⫶C bending ...	8	8	8	8	8	950
4. $\frac{H}{H}$>C—C, $\frac{H}{H}$>C=C, or $\frac{H}{H}$>C⫶C bending	8	11	10	11	10	950
5. C—C stretching	2	4	2	6	3	1000
6. C=C stretching	4	2	—	2	—	1600
7. C⫶C stretching	—	—	4	—	4	1335
8. C=C—C, C⫶C—C, or C—C—C bending ...	4	—	4	—	4	320
9. C=C—C or C—C—C bending	—	10 †	—	9	—	190 *
10. C⫶C⫶C bending	—	—	2	—	2	336
β 11. $\frac{H}{H}$>C=C torsion	4	1	—	1	—	570
12. $\frac{H}{H}$>C⫶C torsion	—	—	2	—	2	—
13. C⫶C torsion	—	—	2	—	2	—
14. C—C internal rotation	2	1	3	1	3	—

† The mode which does not appear in the fully-formed 4-vinyl*cyclo*hexene corresponds to a twisting of four carbon atoms and six hydrogen atoms relative to the rest of the molecule.

The normal modes indicated in lines 1—11 of Table III were treated as harmonic vibrations, but the contributions of the modes referred to in the last three lines were calculated with the help of the formula in line 4 of Table I and the data in Table IV. The reduced moments of inertia, i, relating to the rotation about the bonds

TABLE IV.

Data for Calculation of Contributions due to some of the Torsional Modes.

	Rotation about	$i \dfrac{10^{39}}{\text{g.-cm.}^2}$.	σ_i.		Rotation about	$i \dfrac{10^{39}}{\text{g.-cm.}^2}$.	σ_i
Butadiene	C—C	2 ± 0·5	1		C⫶C and C⫶C ₇ ₈	0·3 ± 0·2	2
Cyclic activated complex	C—C (vinyl group)	27 ± 3	1	Open-chain activated complex	C⫶C and C⫶C ₂ ₃ ₆ ₇	4 ± 2	1
					C—C and C—C ₃ ₄ ₅ ₆	6 ± 2	1
					C—C ₄ ₅	24 ± 8	1

C⫶C and C⫶C of the open-chain activated complex were estimated on the assumption that the C—H
₁ ₂   ₇ ₈
distance is 1·1 A., but the other i values relate to molecular models in which the hydrogen atoms were treated as coinciding with adjacent carbon atoms. All the reduced moments of inertia were calculated both for extended and for closely packed configurations, the figures in cols. 3 and 7 of Table IV being the means of the relevant maximum and minimum values. The mode designated in Table III by " C—C internal rotation " was treated as free internal rotation; a correction due to a restricting potential would not alter any of the following conclusions even if it were assumed that the potential is as high as 3 kg.-cals./mol. The contributions of the modes designated by $\frac{H}{H}$>C⫶C torsion and C⫶C torsion are the means of two sets of values which were obtained by assuming that the bonds between the atoms 1, 2, 3, and 6, 7, 8 of the open-chain activated complex are (*a*) ordinary single bonds and (*b*) ordinary double bonds. In calculating set (*a*), the free rotator treatment was applied and the data in lines 1 and 2 in col. 7 of Table IV were used. Set (*b*), on the other hand, relates to harmonic torsional vibrations and to frequencies which were estimated by allowing for the same force constant as that of the torsional mode in ethylene (cf. papers referred to by Gallaway and Barker, *J. Chem. Physics*, 1942, **10**, 88). This method is somewhat different from that employed by Kistiakowsky and Ransom, who calculated the relevant contributions by applying the harmonic oscillator formula and by estimating the relevant frequency on the assumption that the force constant is one half of that of the torsional vibration of ethylene.

The quantity of $\Delta S^*/R$ of equation (2) can be regarded as being the sum of three terms :

$$\Delta S^*/R = [\Delta S^*_{\text{rig.}} + \Delta S^*_{\text{vib. }(\alpha)} + \Delta S^*_{\text{vib. }(\beta)}]/R \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $\Delta S^*_{\text{rig.}}/R$ comprises the contributions of the various species supposed to be rigid, and $\Delta S^*_{\text{vib. }(\alpha)}/R$ and $\Delta S^*_{\text{vib. }(\beta)}/R$ relate respectively to the stiff vibrations listed in Part α of Table III and to the looser vibrations and internal rotations mentioned in Part β. The various contributions to $[\Delta S^*_{\text{rig.}} + \Delta S^*_{\text{vib. }(\alpha)}]/R$ are in Table V, those to $[\Delta S^*_{\text{vib. }(\beta)}]/R$ are in Table VI, and a summary of all the numerical results of the entropy

TABLE V.

Contributions to $[\Delta S^*_{rig.} + \Delta S^*_{vib. (a)}]/R$ ($T = 600°$).

Freedom.	2 Butadiene.	Activated complex.	
		Cyclic.	Open-chain.
Translation (relating to g.-mol. and cm.³)	20·0	11·0	11·0
External rotation	24·2 ± 0·8	15·2 ± 1	14·0 ± 1·5
Vibration (a)	7·8	9·4	9·5
Sum	52·0	35·6	34·5

TABLE VI.

Contributions to $\Delta S^*_{vib. (\beta)}/R$ ($T = 600°$).

Freedom.	2 Butadiene.	Activated complex.	
		Cyclic.	Open-chain.
C=C—C, C=C—C, or C—C—C—C bending	5·1	20·1	5·1
C=C=C bending	—	—	2·5
$\underset{H}{\overset{H}{>}}$C=C torsion	3·2	0·8	—
$\underset{H}{\overset{H}{>}}$C=C torsion	—	—	3·1
C=C torsion	—	—	7·6
C—C internal rotation	7·8 *	4·1	10·9
Sum	16·1	25·0	29·2

* It follows from this value and from the figure in the first line of Table V that $(S_{rig.} + S_{C-C\ internal\ rotation})/R = 52\cdot0$ for two butadiene molecules, which agrees with Kassel's computation (*J. Chem. Physics*, 1936, **4**, 435); it should be noted that in the above tables $S_{translation}$ relates to g.-mols. and cm.³, whereas Kassel's translational entropy relates to 1 atm.

TABLE VII.

Summary of Numerical Results of Entropy Calculations ($T = 600°$).

	Activated complex.		
	Cyclic.	Open-chain.	Comment.
$[\Delta S^*_{rig.} + \Delta S^*_{vib. (a)}]/R$	−16·4	−17·5	⎫
$\Delta S^*_{vib.(\beta)}/R$	+ 8·9	+13·1	⎬ Present computation.
$\Delta S^*/R$ .... $\Big\{$	− 7·5	− 4·4	⎭
	−16·7	− 8·6	Kistiakowsky and Ransom.

calculations is in Table VII. It should be noted that the difference between the two values in the first line of Table VII is smaller than the inaccuracy due to the incomplete knowledge of the principal moments of inertia. The means of the two sets of $\Delta S^*/R$ values listed respectively in line 3 and 4 of Table VII are :
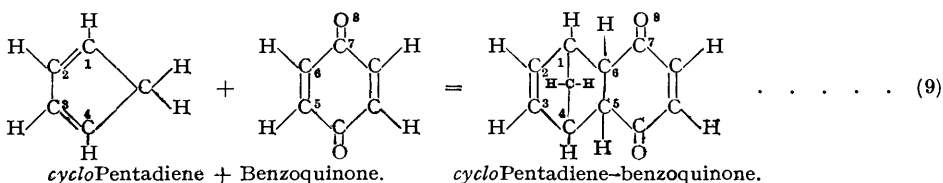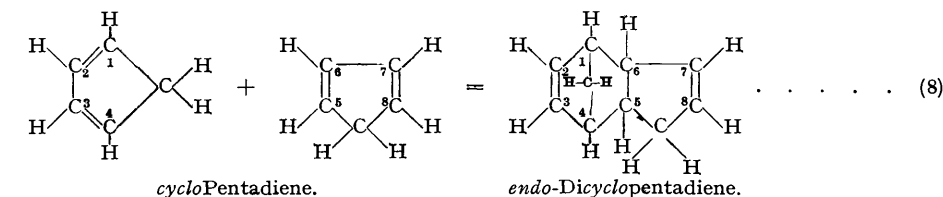
$$\Delta S^*/R = -12 \pm 5 \text{ for cyclic activated complex} \quad . \quad . \quad . \quad . \quad . \quad (5)$$
$$\Delta S^*/R = -6 \pm 3 \text{ for open-chain activated complex} \quad . \quad . \quad . \quad . \quad (6)$$

It follows from Kistiakowsky and Ransom's kinetic measurements that the non-exponential A factor of equation (2) is $10^{9\cdot96 \pm 0\cdot18}$ cm.³/g.-mol. sec., so that

$$\Delta S^*_{exptl.}/R = 2\cdot30\ (9\cdot96 - \log_{10} \kappa - \log_{10} kT/h - 2 \log_{10} e) \quad . \quad . \quad . \quad . \quad (7)$$

If the transmission coefficient κ is assumed to be unity $\Delta S^*_{exptl.}/R$ would equal $-9\cdot2 \pm 0\cdot5$ at $T = 600°$, which is compatible with both (5) and (6). Thus the theoretical method cannot be used in order to find out whether the dimerisation of butadiene or the reverse decomposition of 4-vinyl*cyclo*hexene involves the transient formation of open-chain radicals. It is possible, however, that entropy calculation will lead to more conclusive results if new spectroscopic and thermochemical data relating to the participants of reaction (1) should become available.

$$\text{. . . . . . (8)}$$

*cyclo*Pentadiene.   *endo*-Di*cyclo*pentadiene.

$$\text{. . . . . (9)}$$

*cyclo*Pentadiene + Benzoquinone.   *cyclo*Pentadiene–benzoquinone.

Arguments against a Mechanism involving Free Radicals.—The dimerisation of butadiene is chemically and kinetically of the same type as the diene syntheses (8) and (9).   If the mechanism of these associations is stepwise, then the structure of the rate-determining activated complexes might be as in (II) or (III).

(II.)

(III.)
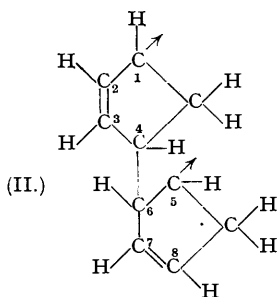
Radical II.   Formation of a bond between the carbon atoms 1 and 5 leads to *endo*-di*cyclo*pentadiene.
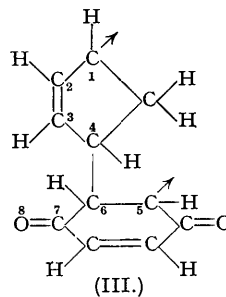
Radical III.   Formation of a bond between the carbon atoms 1 and 5 leads to *cyclo*pentadiene–benzoquinone.

The associations (8) and (9) involve relatively complex molecules and, therefore, a sufficiently accurate *a priori* calculation of the entropy of activation is more difficult than in the case of reaction (1).   There is, however, a qualitative method of approach in order to gain information about the nature of intermediates in all these diene syntheses which refers to an interpretation of the results of rate measurements carried out both in the presence of a relatively large amount of oxygen or peroxides and under conditions under which these latter substances were excluded from the reaction mixture as far as possible.   The following observations were made in these experiments.

Reactions of butadiene which occur wholly in the gas phase.   Vaughan (*J. Amer. Chem. Soc.*, 1932, **54**, 3863) treated butadiene with hexaphenylethane in order to remove the last traces of oxygen or peroxides, but this had no measurable influence on the rate of the low-molecular polymerisation, the course of this process being followed by measuring the pressure change at constant volume.   In one experiment at 646° K. a relatively large amount of oxygen was added to the reaction mixture, with the result that the rate of pressure change increased by about 30%.   The present author believes that this oxygen effect does not relate to the dimerisation of butadiene but to consecutive reactions of higher activation energy.*   If this assumption is correct, it would be expected that at a lower temperature the oxygen influence is less pronounced because under the latter conditions the observed pressure change is more closely related to the dimerisation reaction.   Kistiakowsky and Ransom (*loc. cit.*, Table II) found, in fact, that at a temperature which was 119° lower than that obtaining in Vaughan's experiment catalysis by molecular oxygen could not be detected.

Homogeneous reactions of liquid butadiene.   Koblianski and Piotrovski (*Synt. Kauchouk*, 1936, **5**, No. 3, 3) did a series of measurements from which it follows that the macropolymerisation of butadiene is accelerated by oxygen,† while the rate of the dimerisation process is not detectably altered.   It appears, therefore, that the primary steps in the macro-polymerisation and in the dimerisation of butadiene are fundamentally different, and that the formation of 4-vinyl*cyclo*hexene should not be regarded as a side reaction of the low-molecular link of a polymerisation chain.‡

Dimerisation of cyclopentadiene and addition of cyclopentadiene to benzoquinone.   Stobbe and Reuss (*Annalen*, 1912, **391**, 151), Schultze (*J. Amer. Chem. Soc.*, 1934, **56**, 1552), Harkness, Kistiakowsky, and Mears (*J. Chem. Physics*, 1937, **5**, 682), Benford, Kaufmann, Khambata, and Wassermann (J., 1939, 362, 375, 381), and Raistrick, Sapiro, and Newitt (*ibid.*, p. 1764) found that the rate of these associations is not influenced by oxygen or by peroxides, the various experiments being carried out between 287 and 450° K. and between 1 and 4,000 atm.

Species such as (I), (II), or (III) should combine quickly with molecular or peroxide oxygen, these reactions being probably faster than the oxidation of the alternative type of activated complexes.   If, therefore, the transient formation of diradicals played a rôle, oxygen or peroxide should produce a marked change of the course of the overall associations.   Since an effect of this kind has not been observed, it seems on the whole more justifiable to assume that the rate-determining step of bimolecular diene syntheses involves activated complexes which are stereochemically similar to the fully formed products.

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Imperial College and University College, London.

* Kistiakowsky and Ransom refer to one of the possible consecutive reactions, *viz.*, the addition of butadiene to 4-vinyl-Δ³-*cyclo*hexene to produce Δ³ ⁚ ³'-octahydrodiphenyl.   The activation energy of this process is assumed to be 38 kg.-cals., whereas that of the dimerisation of butadiene amounts to 23·7 kg.-cals.   Δ³ ⁚ ³'-Octahydrodiphenyl was isolated in the liquid state, in the presence of acetylenedicarboxylic acid in a yield of 5% of the theoretical amount (Alder and Rickert, *Ber.*, 1938, **71**, 373).   There is no evidence that under the conditions of the experiments of Kistiakowsky and Ransom the consecutive reactions referred to above include the 1 ⁚ 4–1 ⁚ 2 addition of butadiene and 4-vinyl*cyclo*hexene.

† It is possible that the oxygen effect is related to the irreversible formation of oxidised polybutadienes·   cf. Chochlovkin, *Synt. Kauchouk*, 1936, **5**, No. 4, 12.

‡ This conclusion is in agreement with observations made by Saveliev, Arbirdan, and Zlatogurski (*Synt. Kauchouk*, 1936, **5**, No. 4, 18), who found that copper naphthenate and copper oleate are inhibitors in the macro-polymerisation of butadiene, but that they do not affect the rate of the dimerisation reaction.