190. *The Mechanism of Additions to Double Bonds. Part I. Thermochemistry and Kinetics of a Diene Synthesis.*

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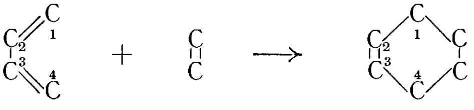
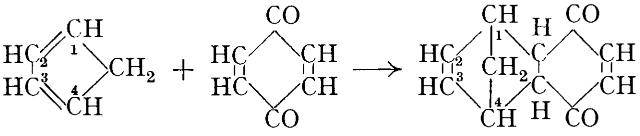
THE important example of 1 : 4-addition to a conjugated system (*a*), known as a diene synthesis, where the addendum is a compound containing a reactive double bond (*b*), was



(*a*.) (*b*.) (*c*.)

investigated chiefly by Diels and Alder. The present communication attempts to provide an explanation why addition should not occur also in the 1 : 2-position, the typical case investigated being the reaction between *cyclo*pentadiene (I) and benzoquinone (II) to afford *cyclo*pentadienebenzoquinone (III).*



(I.) (II.) (III.)

Section 1 deals with the determination of the heat of the 1 : 4-addition of benzoquinone to *cyclo*pentadiene, and also with that of the hypothetical 1 : 2-addition. Both reactions are exothermic, and there is therefore no thermodynamic reason for the preferential 1 : 4-addition. In Section 2, the kinetics of the reaction are investigated, and it is shown that a second-order association, relatively insensitive to catalysts, light, or magnetic field, is involved. The activation energy in alcohol or benzene is 13—14 kg.-cals. Section 3 gives the calculation of the dipole induction energy for different mutual orientations of the *cyclo*pentadiene and the benzoquinone molecule. For orientations which might lead to the 1 : 4-addition product, the induction energy is greater than for those suitable for 1 : 2-addition. Hence, the conclusion is drawn that the activation energy of the 1 : 2-addition is greater than that of the 1 : 4-addition, and that this is the explanation for the observed course of the reaction.

The method employed here will, of course, not be applicable to the general case of addition of double bonds to conjugated systems if all the dipole moments of the bonds of the reacting molecules are immeasurably small (*e.g.*, dimerisation of *cyclo*pentadiene). If, however, the reacting molecules contain, like benzoquinone, polar groups (*e.g.*, maleic anhydride), then a calculation of the induction energies will in many cases be useful.

1. *Thermochemistry of the* cyclo*Pentadiene–Benzoquinone Reaction.*

In order to determine the heat of the additive reaction, the heats of formation of the three molecules from carbon (^5S),† hydrogen, and oxygen must be known. For the calculation of the heats of formation from the heats of combustion (corrected for the gaseous state) the heat of the reaction $C(^5S) + O_2 = CO_2$ was taken as 270 kg.-cals. (cf. Kohn and Guckel, *Z. Physik*, 1924, **27**, 306; Heitler and Herzberg, *ibid.*, 1929, **53**, 52; Pauling, *J. Amer. Chem. Soc.*, 1932, **54**, 3570; Pauling and Sherman, *J. Chem. Physics*, 1933, **1**, 606).

The bond energies given by Pauling and Sherman (*loc. cit.*) were used for the additive calculation of the heats of formation. For the C=O bond in quinone and in (III), however, another value, *viz.*, 183 kg.-cals. was taken. This figure is an average of the C=O value given by Pauling and Sherman and of that of six cyclic ketones (suberone, β-methyl*cyclo*hexanone, β-methyl*cyclo*pentanone, *cyclo*pentanone, and *cis*- and *trans*-β-decalone).

The heat of combustion of gaseous *cyclo*pentadiene was found to be 707 ± 7 kg.-cals./mol. (see p. 839), whence the heat of formation is 1153 ± 7 kg.-cals., whereas addition according to 2(C=C) + 3(C—C) + 6(C—H) leads to 1152 kg.-cals. The resonance energy of a system of two conjugated double bonds is 8 kg.-cals. according to Pauling and Sherman (*loc. cit.*, p. 682). This value is probably too high, for the heats of formation of butadiene and isoprene calculated from the heats of combustion (Landolt–Börnstein–Roth, "Tabellen," II, Suppl.) are, if anything, a little lower than those obtained by adding the bond-energies. The close agreement between the calculated and the found heat of formation of *cyclo*pentadiene is probably fortuitous.

In correcting the heat of combustion of solid benzoquinone ("Tabellen," I, Suppl.) for the gaseous state, the heat of sublimation given by Coolidge and Coolidge (*J. Amer.*

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* For formation and constitution of this compound, see Albrecht, *Annalen*, 1906, **348**, 1; Diels, Blom, and Koll, *ibid.*, 1925, **443**, 247; Diels and Alder, *ibid.*, 1928, **460**, 98; Diels, Alder, and Stein, *Ber.*, 1929, **62**, 2337; Alder and Stein, *Annalen*, 1931, **485**, 218; 1933, **501**, 253.

† The exact description of the electronic state of quadrivalent carbon is $2s2p^3\ ^5S$.

Chem. Soc., 1927, **49**, 103) was used. The experimental heat of formation is 1405 kg.-cals., and the value calculated from $2(C{=}O) + 2(C{=}C) + 4(C{-}C) + 4(C{-}H)$ is 1403 kg.-cals.

The heat of combustion of (III) was found to be 1336 ± 1 kg.-cals./mol. (see p. 839). The heat of sublimation of quinone is 15 kg.-cals., and the heat of vaporisation of *cyclo*pentadiene 7 kg.-cals. (Trouton). It can be assumed that the heat of sublimation of (III) is 22 ± 5 kg.-cals., for Dunkel (*Z. physikal. Chem.*, 1928, **138**, 44) has pointed out that the molecular forces of certain types of organic compound are additive, and this can be explained by a theoretical treatment of cohesion forces given by London (*Z. Physik*, 1930, **63**, 245; *Z. physikal. Chem.*, 1930, *B*, **11**, 222). The heat of combustion of the gaseous addition compound is therefore 1358 ± 6 kg.-cals., and this gives a heat of formation of 2579 ± 6 kg.-cals., whereas addition according to $2(C{=}C) + 11(C{-}C) + 10(C{-}H) + 2(C{=}O)$ leads to 2589 kg.-cals. The difference of 10 ± 6 kg.-cals., if real,* is doubtless connected with the ring-strain in *bicyclo*heptene systems. Alder and Stein (*Ber.*, 1934, **67**, 613) deduce for similar compounds a ring-strain of 6—7 kg.-cals.

The compound (III) contains a system of three conjugated double bonds $O{=}C{-}C{=}C{-}C{=}O$. A comparison of the experimental and the calculated heat of formation of methyl fumarate shows that such a system has no thermochemically measurable resonance-energy : $2(C{-}C) + (C{=}C) + 8(C{-}H) + 2(C{=}O)$ † $+ 4(C{-}O) + 2$(resonance energy CO_2Me) ‡ = 1859 kg.-cals.; experimental heat of formation (cf. Wassermann, *Z. physikal. Chem.*, 1930, **140**, 419) = 1857 kg.-cals. Table I summarises the numerical details.

TABLE I.

Experimental and calculated heats of formation of cyclo*pentadiene* (I), *benzoquinone* (II), *and* cyclo*pentadienebenzoquinone* (III).

	Heat of combustion, corr. for gaseous state (kg.-cals./mol.).	Heat of formation from $C(^5S)$, H, and O, kg.-cals.		Remarks.
		From heat of combustion.	From bond-energies.	
(I)	707 ± 7	1153 ± 7	1152	No resonance-energy.‡
(II)	672 ± 1	1405 ± 1	1403	No resonance-energy.
(III)	1358 ± 6	2579 ± 6	2589	No resonance-energy; ring-strain.

‡ Comparison of found and calculated heats of formation of isoprene and butadiene.

From Table I it can be seen that the calculated and the found heats of formation agree within the possible experimental error if allowance is made for the ring-strain in (III). By using this result, the heat of the reaction *cyclo*pentadiene (gas) + benzoquinone (gas) = *cyclo*pentadienebenzoquinone (gas) can be estimated as follows : Energy gain = $2(C{-}C)$; energy consumption = $2[(C{=}C) - (C{-}C)]$ + ring-strain in *cyclo*pentadienebenzoquinone; heat of reaction = difference = 24 kg.-cals. As the heats of formation of certain gaseous endo- and exo-isomeric compounds are nearly identical (Alder and Stein, *Ber.*, 1934, **67**, 613), it is very probable that this heat of reaction is independent of the steric configuration of the product.

A similar calculation for the heat of the hypothetical 1 : 2-addition product requires the thermal equivalent of the ring-strain in the *cyclo*butane ring. There are four liquid *cyclo*butane derivatives whose heats of combustion are known, *viz.*, *cyclo*butylcarbinol, acetyl*cyclo*butane, *cyclo*butanecarboxylic acid, and methyl *cyclo*butane-αβ-dicarboxylate (cf. Landolt–Börnstein–Roth, "Tabellen"; Beilstein, Vol. V, Erg.-bd., p. 5, note 1). For the additive calculation of the heats of formation, the bond strengths and the resonance energy for the carboxyl and the carbomethoxy-group given by Pauling and Sherman (*loc. cit.*) were used. Comparison with the experimental heats of formation gives about 15 kg.-cals. (average) for the ring-strain in the *cyclo*butane ring. By taking this value and calculating as before, the following result is obtained : *cyclo*pentadiene (gas) + benzoquinone (gas) = hypothetical 1 : 2-addition product (gas) + 19 kg.-cals.

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* The conclusion reached above is independent of the possibility of the thermochemical determination of the ring-strain in (III).

† 178 Kg.-cals.

‡ Cf. Pauling and Sherman, *loc. cit.*

The absolute values of the calculated heats of reaction are, of course, only a very rough approximation. The energy difference between C^3P and C^5S, which was employed in the calculation, is not accurately known. Heitler and Herzberg's value (*loc. cit.*) which was used seems to be much too small (cf. van Vleck, *J. Chem. Physics*, 1934, **2**, 20, 297). Further, a possible change of the zero-point energy of the system before and after the addition process should be considered for a more accurate calculation. The comparison of the values for the heat of 1 : 4- and 1 : 2-addition, however, is not much affected by these uncertainties, and the calculation shows, therefore, that both the 1 : 4- and the 1 : 2-addition of benzoquinone to *cyclo*pentadiene are exothermic. This might have been expected from a study of the models, as the ring-strain in the *cyclo*butane ring is nearly the same as in camphor (cf. Freudenberg, "Stereochemie," 1933, p. 790), which contains an *endo*methylene bridge similar to that in (III).

The assumption that the equilibrium between *cyclo*pentadiene, benzoquinone, and their hypothetical 1 : 2-addition product lies far on the side of dissociation is therefore so improbable that it cannot be used to explain the actual course of the reaction.

2. *Kinetics of the* cyclo*Pentadiene–Benzoquinone Reaction.*

The following reactions have to be considered in a mixture of quinone and *cyclo*pentadiene in the presence of air :

(i) (I) + (II) ⟶ (III); (ii) (III) ⟶ (I) + (II); (iii) (III) + (I) ⟶ di*cyclo*pentadienebenzoquinone (Albrecht, *loc. cit.*); (iv) 2(I) ⟶ di*cyclo*pentadiene (cf. Alder and Stein, *Annalen*, 1933, **504**, 316); (v) (I) + O_2 ⟶ *cyclo*pentadiene oxide (Engler and Frankenstein, *Ber.*, 1901, **34**, 2938).

In a preliminary communication (*Ber.*, 1933, **66**, 1392), it was shown that the velocity coefficient of reaction (i) at 20° is, according to the solvent, 0·002—0·2 l./g.-mol./sec., and that the rate of (iii) in benzene solution is about 100 times smaller. Further, a series of measurements (Stobbe and Reuss, *Annalen*, 1901, **391**, 151; Barret and Burrage, *J. Physical Chem.*, 1933, **37**, 1029; Schulze, *J. Amer. Chem. Soc.*, 1934, **56**, 1552) shows that the rate of (iv) is about 10^4 times smaller than that of (i). Reaction (v) is still slower than (iv) (cf. Stobbe and Dünnhaupt, *Ber.*, 1919, **52**, 1436). In order to obtain information as to the relative rate of reaction (ii), the amount of benzoquinone used during the attainment of a steady state in an equimolar mixture of it with *cyclo*pentadiene was measured. At 20°, 40°, and 50°, 96—99% of the benzoquinone used was found to have reacted. *cyclo*-Pentadienebenzoquinone is known to isomerise easily. This is connected with the mobility of the γ-hydrogen atoms (Diels, Alder, and Stein, *loc. cit.*), and also possibly with the wandering of double bonds without migration of hydrogen atoms and with steric changes. On this account, in addition to the foregoing determination, the *cyclo*pentadienebenzoquinone formed (under the conditions of the kinetic measurements) was also isolated; the yield was 92—94% of the theoretical.

As benzoquinone is much more highly coloured than the product (III), the course of the additive reaction can be followed colorimetrically (cf. Wassermann, *Nature*, 1934, **134**, 101), and it was found to be of the second order (time for half-change inversely proportional to equimolar initial concentration). The velocity coefficients (*k*) given in Table II are accurate to within 5—7%, and the critical increments as quoted below to about ± 1 kg.-cal.

TABLE II.

Velocity coefficients and half-change periods (*at* 20·4°).

Solvent.	Initial concn., g.-mol./l. (II).	(I).	*k*, l./g. mol./sec.	Half-change, sec. × 10^{-2}.	Solvent.	Initial concn., g.-mol./l. (II).	(I).	*k*, l./g. mol./sec.	Half-change, sec. × 10^{-2}.
C_6H_6	0·0500	0·0500	0·0072	28	EtOH	0·0100	0·0100	0·030	34
	0·0200	0·0200	0·0067	75		0·0100	0·00330	0·028	27
	0·0200	0·0100	0·0065	62		0·00500	0·00500	0·030	67
	0·0100	0·0100	0·0067	150		0·00200	0·00200	0·030	168
	0·00200	0·00200	0·0065	768					

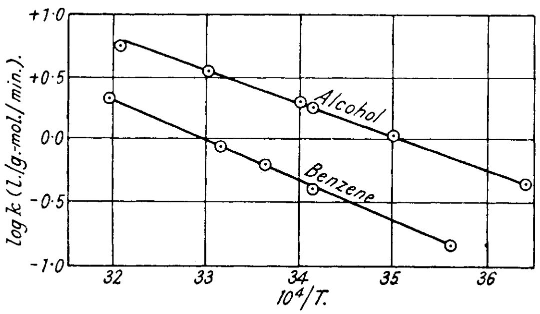
The proportionality of log *k* to $1/T$ is shown in Fig. 1. The constants of the Arrhenius equation, $k = Ze^{-E/RT}$ are :

Solvent.	Z (l./g.-mol./sec.).	E (kg.-cals.).	Solvent.	Z (l./g.-mol./sec.).	E (kg.-cals.).
C_6H_6	$2{\cdot}7 \times 10^8$	14·2	EtOH	$8{\cdot}8 \times 10^7$	12·7

The rate of reaction was not affected by the materials of the walls of the absorption cells, by the purity of the solvents or of the reactants, by light, or by a strong magnetic field. The rate at which the yellow colour in the equimolar mixture of benzoquinone and *cyclo*pentadiene faded was unaffected by the addition of iodine (in the dark or in the light), αα′-dipyridyl, *p*-toluenesulphonic acid, ferric chloride, manganous chloride, cupric chloride, *trans*-stilbene, iodoacetic acid, or bromoacetic acid. Chloroacetic acid, phenol, and hydrochloric acid produced a slight increase of the rate, and pyridine a slight decrease.

It is well known that some additions to double bonds and some polymerisations of ethylene derivatives are chain reactions. However, such reactions are often characterised by bad reproducibility of the kinetic measurements, *i.e.*, by great sensitivity to external influences or to traces of foreign substances. The experimental results therefore make it improbable that the present reaction is a chain reaction. In particular, peroxidic intermediate compounds seem to play no part in the kinetics; for if they did, it might be expected, by analogy with other reactions, that iron, copper, or manganese salts, possibly also αα′-dipyridyl or pyridine, would be efficient catalysts, and even small amounts of phenol or stilbene would inhibit the reaction.

FIG. 1.



Temperature dependence of the velocity coefficients.

3. 1 : 4- *and* 1 : 2-*Addition of Benzoquinone to* cyclo*Pentadiene.*

The kinetic measurements recorded in the preceding section show that the velocity coefficient of the reaction is determined by the two constants Z and E of the Arrhenius equation, which for a given solvent are dependent only on characteristic properties of the reacting molecules. This experimental result justifies the assumption that the velocity coefficient of the hypothetical 1 : 2-addition of benzoquinone to *cyclo*pentadiene is also characterised by only two constants. We therefore have :

$$\left.\begin{array}{ll}\text{1 : 4-addition} \quad . \; . \; . \; . \; . \; . \; . \; . \; . & k_{1:4} = Z_{1:4}\,e^{-E_{1:4}/RT} \\ \text{1 : 2-addition} \quad . \; . \; . \; . \; . \; . \; . \; . \; . & k_{1:2} = Z_{1:2}\,e^{-E_{1:2}/RT}\end{array}\right\} \quad (1)$$

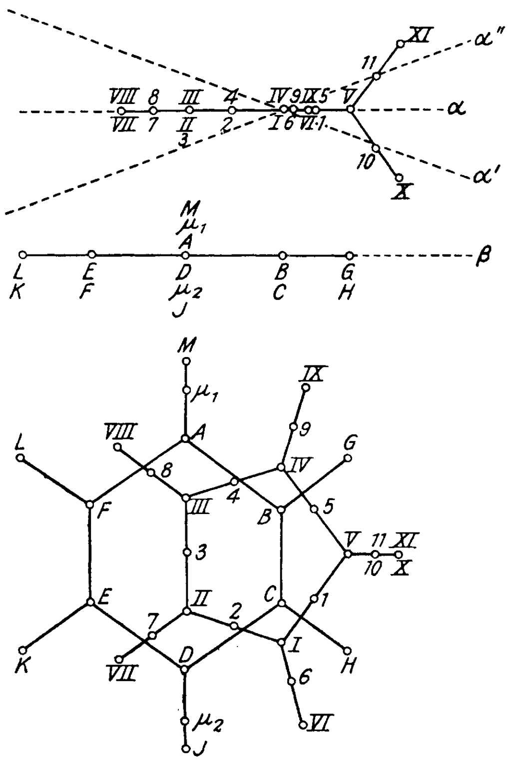
It is necessary for the following considerations to determine the mutual orientations of the benzoquinone and the *cyclo*pentadiene molecules most suitable for the regrouping of the electrons corresponding to the addition. If the C=C bond of the quinone is near the atoms I and IV of the *cyclo*pentadiene, then 1 : 4-addition will result, whereas 1 : 2-addition requires that the C=C bond should be close to the atoms I and II. The juxtaposition of reacting centres is not, however, the sole determining factor. The most suitable orientations will be those in which mutual interpenetration of the outsides of all the other atoms of the reactants occurs to a minimum extent. Figs. 2—4 show such orientations drawn to scale in plan and side-elevation. The lengths of the individual bonds have been taken to be the same as those determined for isolated molecules.

1 : 4-*Addition.*—If the distance *B*IV in Fig. 2 is 2·0 Å., then the distance *G*X or *H*X is 1·72 Å. and *B*X or *C*X 1·90 Å. The orientation of Fig. 3 is also possible; the distance *B*IV being assumed to be, as in Fig. 2, 2·0 Å., then the distance *E*X or *F*X would be 1·6 Å. The steric course of the reaction depends on whether the orientation of the reacting molecules at the moment of impact is that of Fig. 2 or of Fig. 3. This, of course, only holds

when the possibility of a subsequent rearrangement of the incompletely stabilised product is excluded. The interesting subject of *endo-exo*-isomerism of the addition compound is, however, not regarded as within the scope of this paper.

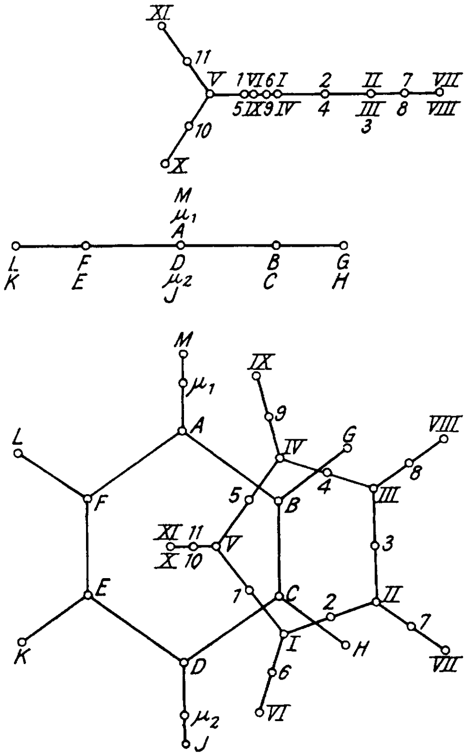
Rotation of the *cyclo*pentadiene about an axis passing through I–IV (Fig. 2) would soon meet with considerable resistance, as repulsive forces between atoms increase rapidly with decreasing distance. For instance, if the diene is rotated through 20° into the plane α', then the distance *H*X or *G*X becomes 1·3 Å. Again, an equal rotation into the plane α'' decreases the distances *E*VII and *F*VIII to 1·4 Å. and *D*II and *A*III to 1·7 Å. Considerations of this nature apply to other *B*IV distances and to the orientation of Fig. 3. Therefore, mutual orientations of *cyclo*pentadiene and benzoquinone suitable for 1 : 4-addition are improbable when the angle between the planes α' or α'' and β is greater than about 20°, and the most favourable orientations will be those in which the planes of the rings are nearly parallel.

FIG. 2.



An orientation suitable for 1 : 4 *addition.*

FIG. 3.



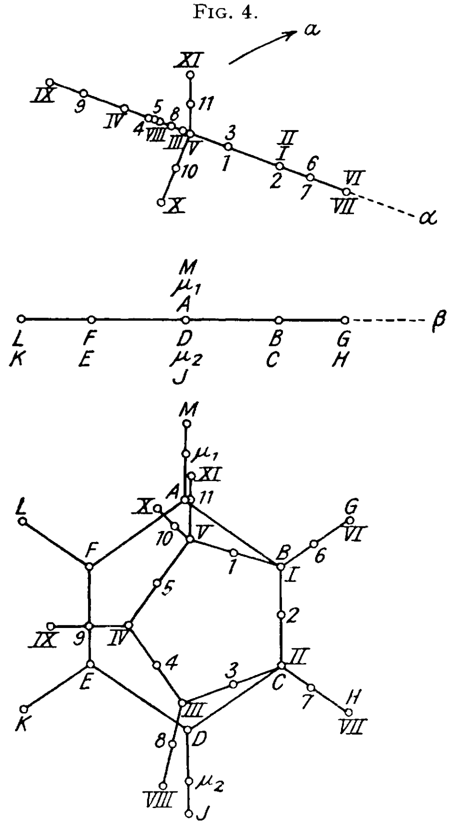
Alternative orientation suitable for 1 : 4 *addition.*

1 : 2-*Addition.*—In the orientation of Fig. 4, the angle between the planes α and β is 20°, and the distance *B*I or *C*II 2·0 Å. The distance *G*VI or *H*VII is 1·75 Å., and *A*X is 1·55 Å. Any material decrease in the angle between α and β is not possible, for the repulsive forces between *A* and X would certainly increase rapidly as soon as *A*X becomes smaller than about 1·4 Å. An increase in the angle would, however, be less strongly resisted than in the orientation of Fig. 2. Rotation of the *cyclo*pentadiene through 160° (in the direction of the arrow *a*) about an axis passing through I–II leads to another orientation suitable for 1 : 2-addition.

Different values of *Z* (equation 1) for two such similar reactions as the 1 : 4- and the 1 : 2-addition could, when both reactions occur in the same solvent, be ascribed only to steric differences. The above discussions of the possible mutual orientations show, therefore, that $Z_{1:2}$ cannot be much smaller than $Z_{1:4}$, and that a difference in the Z values cannot therefore be used to explain the predominance of 1 : 4-addition actually found.

In attempting to base an explanation on a difference between the activation energies $E_{1:2}$ and $E_{1:4}$, it is assumed that benzoquinone and *cyclo*pentadiene first take up an intermediate configuration (transition complex) which can then either decompose into the components, or else give rise to the reaction products by a spontaneous regrouping of the electrons. The smallest energy increment necessary to produce the intermediate configuration can be taken as the activation energy of the reaction.

FIG. 4.



An orientation suitable for 1 : 2 *addition.*

The electrons of the double bond BC are doubtless rendered so mobile by the proximity of the two carbonyl groups that a regrouping of electrons can occur at relatively large separations of the molecules.* This effect will be the same whether the benzoquinone is added in the 1 : 4- or in the 1 : 2-position of the *cyclo*pentadiene. The next step, therefore, is to consider the influence of the carbonyl group, not on the bonds of the quinone, but on the various bonds of the *cyclo*pentadiene. The two dipoles of the carbonyl groups will induce other dipoles, and this will effect a certain attraction between the benzoquinone and the *cyclo*pentadiene molecules.

In order to calculate the energy corresponding to this dipole induction in the positions of Fig. 2 and Fig. 4, the following assumptions were made: the dipole moment of the carbonyl group in benzoquinone is $2{\cdot}8 \times 10^{-18}$ e.s.u. and is localised symmetrically between the imaginary circumferences (cf. Smallwood and Herzfeld, *J. Amer. Chem. Soc.*, 1930, **52**, 1910) of the carbon and the oxygen atoms at the points μ_1 and μ_2; there is no measurable permanent dipole moment corresponding to the C–H bonds of the cyclic molecules involved; the bonds of the *cyclo*pentadiene are treated as polarisable spheres located in the middle of each bond at the points 1–11; the polarisability is isotropic; the dipoles induced in the various bonds have no action on one another. J, the induction energy is given by

$$J = PF^2/2 \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

The polarisability P is obtained from the octet refractions (Smyth, *Phil. Mag.*, 1925, **50**, 301; Fajans and Knorr, *Ber.*, 1926, **59**, 249):

Bond.	C—C.	C=C.	C—H.
$P \times 10^{24}$ (cm.^{3})	0·478	1·64	0·671

In calculating the electric intensity F at the points m (m = 1–11 in Fig. 2 and Fig. 4), the x-axis was chosen to pass through μ_1 and μ_2, while the y-axis lay in the μ_1–μ_2–m-plane (cf. Fig. 5). The following equations hold for F_x and F_y (cf. Jeans, "Electricity and Magnetism," Cambridge, 1925; Smallwood and Herzfeld, *loc. cit.*):

$$\left.\begin{aligned} F_x &= \frac{\mu_1}{r_1^3}(3\cos^2\delta_1 - 1) - \frac{\mu_2}{r_2^3}(3\cos^2\delta_2 - 1) \\ F_y &= \frac{3\mu_1}{r_1^3}\sin\delta_1\cos\delta_1 + \frac{3\mu_2}{r_2^3}\sin\delta_2\cos\delta_2 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

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* Of course the separation will also depend on the mobility of the electrons of the *cyclo*pentadiene.

The induction energies as calculated by (2) and (3) are given in Table III for different distances d characterising the degree of separation of the molecules. Measures for these distances are BIV (= CI) in Fig. 2 and BI (= CII) in Fig. 4.

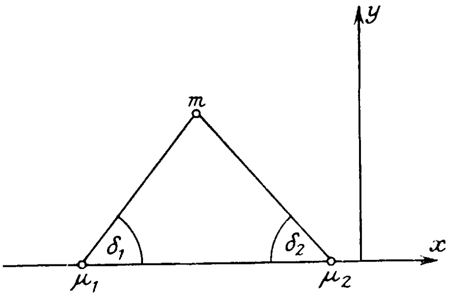
Table III.

Induction energies corresponding to different intermediate configurations in the cyclo*pentadiene–benzoquinone reaction.*

1 : 4-Addition, intermediate configuration, Fig. 2	Distance d (Å.)	2·33	2·00	1·80
	Induction energy (kg.-cals./mol.)	−3·3	−6·7	−9·6
1 : 2-Addition, intermediate configuration, Fig. 4	Distance d (Å.)	2·33	2·00	1·80
	Induction energy (kg.-cals./mol.)	−2·4	−3·7	−5·1

In order that the reacting molecules may approach one another so closely that addition can take place, considerable repulsive forces have to be overcome by the help of kinetic energy of translation, dispersion forces (cf. London, *loc. cit.*), and induction energy. The figures of Table III show that the induction energy is greater for that orientation which will result in 1 : 4-addition than for that giving 1 : 2-addition. We assume that the dispersion forces in the orientation of Fig. 4 are not greater than in that of Fig. 2.* It then seems reasonable to conclude from the calculated induction energies that the activation energy is greater for the 1 : 2- than for the 1 : 4-addition and that, as a first approximation, the difference in the activation energies equals the difference in the induction energies. If it be further assumed that in equations (1) $Z_{1:2} = Z_{1:4}$, then the following ratios of the velocity constants are obtained from the data in Table III :

Fig. 5.



In equation (3) *the distance* $r_1 = \mu_1 m$ *and* $r_2 = \mu_2 m$.

Distance d (Å.)	2·33	2·00	1·80
$k_{1:4} : k_{1:2}$ at 20°	~5	~170	~2200

The differences in the rates calculated from the induction energies are therefore sufficient to explain the predominant formation of the 1 : 4-addition product, provided the distance d be not much greater than 2 Å.

Experimental.

The *cyclo*pentadienebenzoquinone used was purified by recrystallisation from methyl alcohol and light petroleum until the colour was constant. Shaking of the light petroleum (b. p. 60—80°) solution with calcium oxide, magnesium oxide, calcium carbonate, Fasertonerde (Merck), sucrose, or charcoal (Merck) then produced no diminution of colour. The colour measurements throughout were carried out with Zeiss's Pulfrich Stufenphotometer and filter S_{47}. The colour is a much more sensitive criterion of the purity of the substance than the m. p.; *e.g.*, two specimens, both of m. p. 76—77°, gave molar extinction coefficients (ε) of 0·122 and 0·144 l./g.-mol./cm. (benzene). The ε value (l./g.-mol./cm.) of the purest specimen was 0·0578 in benzene and ~0·1 in ethyl alcohol. Beer's law holds in both solvents, and at room temperature the colour of a benzene solution remains constant for many hours. In benzene the value of ε was unaffected by temperature changes between 11° and 50°. In alcohol, the colour deepens rapidly. The extinction coefficient was determined as soon as possible after preparation of the solution.

The heats of combustion in Tables IV and V were determined at 20° (cf. p. 839) by using oxygen at 38 atm. in a bomb with a water equivalent of 2806·2 ± 0·6 cals./degree.

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* It will be shown in a later paper that this assumption holds true.

TABLE IV.

Heat of combustion of cyclo*pentadienebenzoquinone.*

Weight, g.	Δt (corr.).	Heat of combustion, cals. Total.	Corr.	Cals./g. (const. vol.).	
0·60750	1·6755°	4701·8	34·9	7682·0	Mean 7677·0
0·60480	1·6630	4666·7	23·9	7676·5	
0·60375	1·6625	4665·3	31·7	7674·5	
0·55760	1·5360	4310·5	30·5	7676·0	

The polymeric *cyclo*pentadiene used for the preparation of the monomeride had been prepared by Fraenkel and Landau (Berlin) and Light (London). An all-glass distillation apparatus with an efficient fractionating column was used. The apparatus was first evacuated and then filled with nitrogen. The distillate, too, was kept in nitrogen. After the second distillation, the b. p. was constant to within a few tenths of a degree, and agreed with the accepted value. Since the combustion took place some 2 or 3 days after the distillation, some polymerisation had occurred. It was therefore necessary to estimate this amount (cf. Stobbe and Reuss, *loc. cit.*; Schulze, *loc. cit.*) by determining the refractive index of a control sample which had undergone exactly parallel treatment. As the heat of combustion of di*cyclo*pentadiene is known (Becker and Roth, *Ber.*, 1934, **67**, 627; Alder and Stein, *loc. cit.*), that of *cyclo*pentadiene can be calculated if the heat of combustion of a mixture of the two in known proportion is determined. In order to calculate the composition of the mixture from $n_D^{22°}$, it is necessary to get $n_C^{20°}$; for this the data of Stobbe and Reuss (*loc. cit.*), v. Auwers (*Ber.*, 1912, **45**, 3078), and Zelinsky and Lewina (*Ber.*, 1933, **66**, 477) were used.

TABLE V.

Heat of combustion of cyclo*pentadiene.*

Sample.	$n_D^{22\cdot0°}$.	Di*cyclo*pentadiene in mixture, %.	Heat of combustion, cals./g. Mixture.	*cyclo*Pentadiene.	
a	1·4937	72·6	10,475	10,570	Mean 10,600 ± 100
b	1·4928	71·5	10,528	10,770	
c	1·4966	76·8	10,441	10,480	

After the combustions, carbon monoxide could not be detected, but a little lamp black was found. However, the heat of combustion of this was only about 0·2% of the total heat of combustion. The uncertainty of the values in Table V is connected with the great volatility of the liquid * and relatively high rate of polymerisation. The determination of the composition of the mixture at the moment of combustion is therefore subject to an error of 1%.

Different specimens of benzoquinone (Kahlbaum, Merck, B.D.H.) were crystallised 1—3 times from hexane and carefully dried. Consistent results were obtained with the different materials. Table VI gives the ε values : Beer's law held for the given range of concentration, and no temperature effect could be observed (see last col.).

TABLE VI.

Molar extinction coefficients of benzoquinone.

Solvent.	ϵ (l./g.-mol./cm.).	No. of concns. investigated.	Range of concn. (g.-mol./l.).	Max. temp. range.
Benzene	17·0	9	0·1—0·0005	8—50°
Alcohol	13·4	8	0·05—0·002	11—40

For the preparation of the *cyclo*pentadiene solutions the ice-cooled distillate was weighed into a measuring flask as quickly as possible. The flask was again cooled with ice, the stopper removed, and the solvent added. The solutions prepared were as dilute as possible and kept at 0°, and were, generally, not more than a few hours old when measured.

In order to obtain the total amount of benzoquinone converted, the extinction coefficient of a solution of equimolar quantities of *cyclo*pentadiene and benzoquinone in the steady state was measured. We have $\alpha_S = (a - x_S)\varepsilon_Q + x_S\varepsilon_C$, where x_S is the amount of quinone reacting, α_S the extinction coefficient in the steady state, and a the initial concentration of benzoquinone or *cyclo*pentadiene : ε_Q and ε_C are the respective molar extinction coefficients of benzoquinone and condensation product.

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* The substance had to be introduced into the bomb in sealed glass bulbs.

TABLE VII.

Amount of benzoquinone used during attainment of a steady state in its equimolar mixture with cyclo*pentadiene.*

Solvent : Benzene.

Temp.	Initial concn. (g.-mol./l.).	Time (hrs.).	a_S (cm.$^{-1}$).	Quinone used, %.
20°	0·0500	620	0·0230	98
20	0·0503	120	0·0409	96
20	0·199	72	0·0435	99
20	0·518	72	0·123	99
20	1·04	100	0·469	98
50	0·310	7	0·130	97

Solvent : Ethyl alcohol.

Temp.	Initial concn. (g.-mol./l.).	Time (hrs.).	a_S (cm.$^{-1}$).	Quinone used, %
20°	0·100	20	0·063	96
20	0·100	120	0·065	96
40	0·110	1	0·076	95
40	0·110	3·5	0·073	96

For the isolation of the product. the solvent was evaporated at room temperature, and the residue crystallised from petroleum (b. p. 60—80°) or from a little methyl alcohol. The m. p. was then 72—75°, not depressed by admixture with pure *cyclo*pentadienebenzoquinone. Repeated recrystallisations of the specimens gave products of m. p. *ca.* 76—77°.

If the mixtures of the reactants were heated at 40° or 50° for periods longer than those indicated in Table VIII (*e.g.*, 20 hrs.), the crystals obtained differed from Albrecht's *cyclo*pentadienebenzoquinone in having greater solubility in methyl alcohol and markedly lower m. p., *viz.*, 55—65° : probably mixtures of isomerides are formed.

TABLE VIII.

Isolation of cyclo*pentadienebenzoquinone.*

Solvent.	Initial concn. of reactants (mol./l.).	Volume (c.c.).	Time (hrs.)	Temp.	Yield, %.
C_6H_6	0·31	100	7	50°	94
EtOH	5·0*	180	24	20—30	92
	0·11	100	2·5	40	93

* Quinone not completely dissolved; concn. refers to total amount.

The velocity constants were calculated from the equations :

$$k = \frac{2{\cdot}30}{(t - t_0)C_\infty} \log_{10} \frac{\alpha(\alpha_0 - \alpha_\infty)}{\alpha_0(\alpha - \alpha_\infty)}$$

$$k = \frac{1}{at} \cdot \frac{\alpha_0 - \alpha}{\alpha - \alpha_0'}$$

In both equations, α, α_0, and α_∞ represent the extinction coefficient at times t, 0, and infinity respectively; α_0' is the extinction coefficient of a *cyclo*pentadienebenzoquinone solution of the concentration a, and C_∞ is the quinone concentration for $t = \infty$.

In carrying out the rate measurements, the quinone solution was kept in a thermostat, and at zero time a *cyclo*pentadiene solution at the same temperature was introduced. The concentrations were so chosen that the volume after mixing differed by not more than 10—15% from the final volume after dilution to the mark. After some minutes the solution was transferred from the measuring flask to the absorption tube, also kept at the same temperature, and the absorption was continuously observed. A typical experiment is given below :

Solvent : alcohol. Thickness, 2·85 cm. Temp., 20·4°. Equimolar initial concentration, 0·0100 mol./l.

t (mins.)	0	26	35	45	56	72	85	101	∞
α (cm.$^{-1}$)	0·134	0·0951	0·0828	0·0744	0·0674	0·0581	0·0540	0·0477	0·001
k (l./g.-mol./min.)...	—	1·7	1·9	1·9	1·7	1·9	1·9	1·9	—

The results of the kinetic measurements are in Table IX. When the mixture was equimolar only one concentration is given; otherwise, the initial concentration of *cyclo*pentadiene is added in brackets. For the constants k, the unit of concentration is g.-mol./l., and time is in mins. The means given in Table II are, however, calculated with the second as the unit of time. The specimens of solvents used (a, b, c, d) are shown in Table X. Some of the experiments were carried out in quartz cells, others in glass cells.

TABLE IX.

Results of kinetic measurements.

Solvent.	Temp.	Initial concn. (g.-mols./l.).	$C_6H_4O_2$ converted, %.	No. of obstns.	*k* (mean).
C_6H_6 (*a*)	20·4°	0·0500 *	75	4	0·43
	20·4	0·0200 *	60	6	0·40
	20·4	0·0200 [0·0100] *	82	4	0·39
	20·4	0·0100 *	75	5	0·40
	20·4	0·0200 †	50	4	0·42
	8·0	0·0200	30	4	0·15
	29·4	0·0100	60	4	0·87
	40·3	0·00500	55	3	2·1
	20·4	0·00200	53	4	0·39
C_6H_6 (*b*)	25·0	0·0200	55	3	0·53
EtOH (*c*) ‡	20·4	0·0100	70	8	1·8
	20·4	0·0100 [0·00330]	76	3	1·7
	20·4	0·00500	53	3	1·8
	20·4	0·00200	50	4	1·8
	2·3	0·0100	40	4	0·44
	11·9	0·0100	62	4	1·1
	21·0	0·00500	40	4	2·0
	30·0	0·00200	60	5	3·6
EtOH (*d*) ‡	39·0	0·00357	65	4	5·6

* The *cyclo*pentadiene solution used was not more than 10 mins. old.
† The 0·04*M*-*cyclo*pentadiene solution was kept at 6° for 2 days before determination.
‡ Benzoquinone solutions freshly prepared before each determination.

TABLE X.

Velocity constants obtained with different specimens of solvents.

Benzene: (*a*) Merck's "zur Analyse"; (*b*) Specimen (*a*) dried for 6 months over Na_2SO_4, then 2 weeks over sodium, and distilled.

Ethyl alcohol: (*c*) Merck's "zur Analyse"; (*d*) "Absolute alcohol" (Burrough), kept for 3 months over CaO, then distilled. Middle fraction, b. p. 78·6°/756 mm.

	(*a*).	(*b*).	(*c*).	(*d*).
k (l./g.-mol./min.)	0·60	0·54	5·8	5·6
Temp.	25°	25°	39·0°	39·0°

The influence of light on the reaction was examined with an Osram "Nitra-Lamp" (220-volt, 500-watt). The filament was placed 35 cm. from the absorption tube containing 0·02*M*-mixtures in benzene at 20°. Experiments were also carried out with a Siemens quartz–cadmium lamp. First, 0·05*M*-solutions of benzoquinone were illuminated in quartz tubes, the windows of the air-bath (see *Nature, loc. cit.*, Fig. 1) also being of quartz. At 20° (layer thickness 2 cm.) in alcohol a marked darkening was observed after 60 mins. In benzene solution, however, no change could be detected after 180 mins.

In alcoholic solutions a slow discoloration is observed, even in the dark, but with the solutions (*c*) and (*d*) the reaction is so slow even at 40° that the kinetic measurements were not disturbed. Mixtures (0·003—0·02*M*) of the reactants in benzene were illuminated with the cadmium lamp at 22—25° (thickness 3—4 cm.) for 200 mins. The image of the arc was projected into the vessel with a quartz condenser; experiments in diffuse light were also carried out. The effect of a magnetic field was examined at 20° in carbon tetrachloride solution with an electromagnet giving a field-intensity of 8900 gauss.

The experiments given in Table XI were carried out in the same way as those of Table IX. The substance added was first mixed with benzoquinone, and then the *cyclo*pentadiene solution was introduced. The comparison absorption tubes were filled with the solvent containing the added substance. It is possible that in Expt. No. 2 a part of the iodine was decolorised, the difference of the extinction coefficients (0·029 cm.$^{-1}$) being without significance. In No. 4 it was shown by titration that no measurable esterification of acid took place. Except for Expts. Nos. 5—7, no influence of the added substances on the colour of the quinone could be found. In Nos. 5—7, the difference in the extinction coefficients after 10 mins. and 40 mins. was determined.

No.	—	5	6	7
Substance added	Nil	$FeCl_3$	$CuCl_2$	$MnCl_2$
$\alpha_{10\text{mins.}} - \alpha_{40\text{mins.}}$ (cm.$^{-1}$)	0·014	0·009	0·015	0·014

The pyridine in Expt. No. 14 was purified by way of its perchlorate.

TABLE XI.

Influence of added substances.

No.	Substance added.	Initial concn. of (I) and (II).	Mol. of added substance per mol. of $C_6H_4O_2$.	Solvent.	Temp.	Time (mins.).	α (cm.$^{-1}$) without added substance.	α (cm.$^{-1}$) with added substance.
1	I (dark)	0·0200	0·01	C_6H_6	25°	62	0·178	0·185
2	I (light)	0·0200	0·01	,,	25	64	0·176	0·147
3	*αα′*-Dipyridyl	0·0200	0·25	,,	25	133	0·141	0·143
4	*p*-$C_6H_4Me{\cdot}SO_3H$	0·00500	16	EtOH	20	40	0·0484	0·0480
5	$FeCl_3$	0·00500	0·4	,,	20	—	—	—
6	$MnCl_2$	0·00500	0·4	,,	20	—	—	—
7	$CuCl_2$	0·00500	0·4	,,	20	—	—	—
8	*trans*-Stilbene	0·00500	0·4	,,	20	40	0·0484	0·0485
9	$CH_2I{\cdot}CO_2H$	0·0200	0·5	C_6H_6	25	30	0·262	0·254
10	$CH_2Br{\cdot}CO_2H$	0·0200	0·5	,,	25	30	0·262	0·244
11	$CH_2Cl{\cdot}CO_2H$	0·0200	0·5	,,	25	30	0·262	0·228
12	PhOH	0·0200	1·3	,,	25	50	0·228	0·186
13	HCl	0·00500	0·5	EtOH	20	40	0·0484	0·0450
14	C_5H_5N	0·0200	1	C_6H_6	25	133	0·145	0·156

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