129. *Homogeneous Catalysis and Solvent Effects in a Diene Synthesis.*

By Albert Wassermann.

The catalytic and solvent effects in a diene synthesis consist in changes of both parameters of the velocity coefficient $Ae^{-E/RT}$, the observed figures suggesting a linear functional relationship between $\log A$ and E. This is explained by using a fundamental equation of the theory of absolute reaction rates in conjunction with a method similar to that described in the preceding paper.

The experiments to be discussed deal with the diene synthesis

*cyclo*Pentadiene + Benzoquinone = *cyclo*Pentadiene–benzoquinone . . . . (1)

the rate of which has been investigated in the presence of trichloroacetic acid, which acts as a homogeneous catalyst (preceding paper) and in different polar and non-polar solvents (Wassermann, *Ber.*, 1933, **66**, 1932; J., 1935, 828; 1936, 1028; *Trans. Faraday Soc.*, 1938, **34**, 128; Fairclough and Hinshelwood, J., 1938, 236; Benford, Kaufmann, Khambata, and Wassermann, J,, 1939, 381). The course of the association can be characterised by second-order velocity coefficients, v, which are represented by the Arrhenius equation

$$v = Ae^{-E/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and it has been found that the catalytic and solvent effects consist in changes of both the non-exponential A factor and the activation energy E.*

In many chemical processes a simple correlation between these two parameters is admittedly not apparent. Fairclough and Hinshelwood (J., 1937, 538; cf. also J., 1938, 236; Hinshelwood, *Trans. Faraday Soc.*, 1938, **34**, 110, 122, 144) showed on the other hand that in the formation of quaternary ammonium salts, in diene synthesis (1), and in certain other reactions the logarithm of the non-exponential A factor increases linearly with the activation energy and they explained the suggested relationship as follows. It is supposed that two colliding particles require on the average a time t after meeting in which to reach the right internal phase for the formation of the product. If a change of chemical conditions produces an increase of certain internal vibrational frequencies of the colliding particles, the time t could be diminished and this would increase the logarithm of the non-exponential A factor. An increase of appropriate vibrational frequencies of the reactants could be connected, on the other hand, with an increase of the force constants of certain bonds which, in turn, could be associated with an increase of the activation energy. In this paper it is shown that the correlation between A and E can be explained not only with the aid of Fairclough and Hinshelwood's theory but also with the aid of a different method, in which the A factor is related to entropy changes rather than to collision frequencies. It is not within the scope of this communication, however, to discuss all those well-established reactions in which the free energy of activation is much less affected by a change of chemical conditions than the energy of activation. The following discussion relates to one example only, *viz.*, to reaction (1), but the results are expressed in a form which makes it easily possible to apply similar considerations not only to associations of the type a + b = (ab), but also to reactions of different stoicheiometric type.

Results and Discussion.—The influence of trichloroacetic acid and that of the various solvents on the kinetics of the formation of *cyclo*pentadiene–benzoquinone is shown by the data of Table I, which also contains the number of runs in each set of kinetic measurements; these were carried out between 2° and 50°, and within this range the temperature-dependence of the two parameters of (2) is smaller than the experimental error.

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* Association (1) is not the only diene synthesis the kinetics of which have been investigated in different solvents. Kaufmann and Wassermann (J., 1939, 870) reported experiments relating to the dimerisation of *cyclo*pentadiene, but in this case the solvent effects were not large enough to produce changes of A and E exceeding the experimental errors.

The initial stage of the trichloroacetic acid catalysis of (1) in benzene solution is kinetically of the third order (cf. preceding paper); for the present purpose, however, the rate is not characterised by third-order catalytic velocity coefficients, v_c, but by second-order velocity coefficients, v, which relate to the overall process (catalysed + non-catalysed association) and are given by $v = v_c c + v_{\text{non-catalysed}}$, where c is the stoicheiometric concentration of the trichloroacetic acid; the velocity coefficient and the non-exponential A factor in the first line of Table I relate to $c = 0{\cdot}0100$ g.-mol./l., *viz.*, to the highest catalyst concentration at which experiments were carried out.

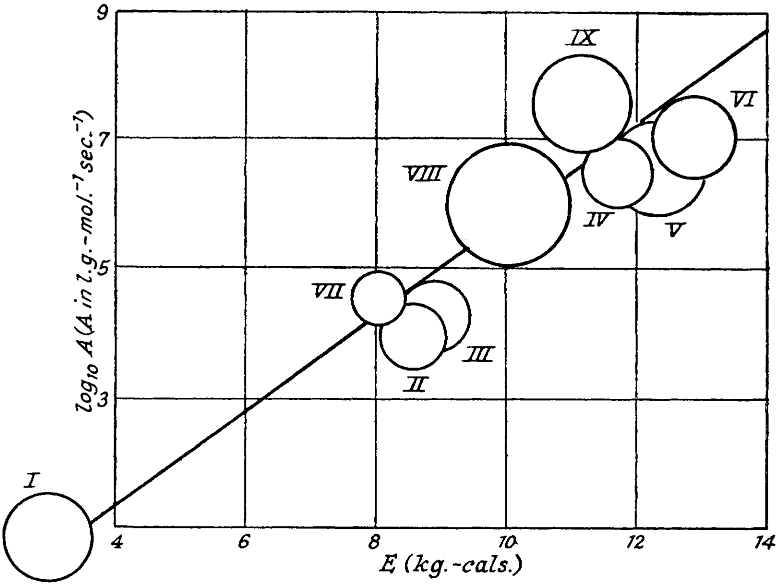
TABLE I.

Catalysis and solvent influence in the formation of cyclo*pentadiene–benzoquinone.*

Measurements in	v (20°).	E.	$\log_{10} A$.	Temp. range.	No. of temps.	No. of runs.
$C_6H_6 + CCl_3{\cdot}CO_2H$	0·03	3·0 ± 1·4	0·9 ± 0·9	13—53°	5	12
CS_2	0·0052	8·5 ± 0·6	4·0 ± 0·6	3—39	7	14
CCl_4	0·0052	8·8 ± 0·4	4·3 ± 0·3	2—50	13	17
C_6H_6	0·0067	11·6 ± 0·4	6·5 ± 0·3	8—50	10	18
n-C_6H_{14}	0·0029	12·1 ± 1	6·5 ± 0·8	20—50	4	12
EtOH	0·030	12·7 ± 0·8	7·0 ± 0·6	2—39	6	9
PhCN	0·048	8·0 ± 0·3	4·5 ± 0·2	10—50	6	6
$PhNO_2$	0·014	10·0 ± 1·2	6·0 ± 1·0	7—50	11	16
$CH_3{\cdot}CO_2H$	0·22	11·0 ± 1	7·5 ± 0·9	10—30	3	6

The parameters E and A in lines 3, 4, and 8 of the table are means of two independent investigations (Fairclough and Hinshelwood; Wassermann; *locc. cit.*); the activation energies and A factors in line 7 were taken from Fairclough and Hinshelwood and all the other figures have been deduced from measurements described in the preceding communications of this series or in the experimental part of this paper. v and A are in terms of g.-mols. and secs., and E in kg.-cals. The suggested linear functional relationship between the figures in cols. 3 and 4 is represented in the figure, the magnitude of the experimental errors being indicated by the diameters of the various circles. The slope of the graph is about 10^{-4} cals.$^{-1}$.

Functional relationship between the parameters of the velocity coefficient.



I, *Trichloroacetic acid in benzene* ; II, *carbon disulphide* ; III, *carbon tetrachloride* ; IV, *benzene* ; V, *hexane* ; VI, *ethyl alcohol* ; VII, *benzonitrile* ; VIII, *nitrobenzene* ; IX, *acetic acid.*

In attempting to explain this correlation between the parameters of equation (2), reference is made to the following fundamental equation of the theory of absolute reaction rates (cf. Evans and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 890; Wynne-Jones and Eyring, *J. Chem. Physics*, 1935, **3**, 492; Eyring, *Chem. Rev.*, 1941, **28**, 308; Laidler, Glasstone, and Eyring, " Theory of Rate Processes," New York, 1941) :

$$v = \kappa(\boldsymbol{k}T/\boldsymbol{h})K^* \quad \ldots \ldots \ldots \quad (3)$$

where κ is the transmission coefficient and the factor K^* relates to the equilibrium

$$cyclo\text{Pentadiene } (a) + \text{Benzoquinone } (b) = \text{Activated complex } (t) \quad \ldots \quad (4)$$

and is defined by

$$K^* = N_t/N_aN_b \quad \ldots \ldots \ldots \quad (5)$$

where N_a and N_b are the number of the reactants per unit volume and N_t is the number of the activated complexes per unit volume and per area h in the phase plane of the reaction co-ordinate and its conjugate momentum. It was stated in the preceding paper that the van't Hoff–Dimroth equation connects the constant of an ordinary chemical equilibrium with the solubilities of both reactants and product molecules. According to Evans and Polanyi and Wynne-Jones and Eyring (*locc. cit.*), a similar correlation exists between the equilibrium factor K^* of the rate equation (3) and the solubilities of the initial state and of the activated complex; it is possible, therefore, to deduce a relationship between the velocity coefficients, the transmission coefficient, and the solubilities, σ, of the participants of such equilibria as (4). For the present purpose this relationship can be written as follows

$$v^{\mathrm{m}}\kappa^{\mathrm{n}}/v^{\mathrm{n}}\kappa^{\mathrm{m}} = \sigma_a^{\mathrm{m}}\sigma_b^{\mathrm{m}}\sigma_t^{\mathrm{n}}/\sigma_t^{\mathrm{m}}\sigma_a^{\mathrm{n}}\sigma_b^{\mathrm{n}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

Here and below, the superscripts m and n indicate that the relevant quantities refer either to the various pure solvents or to the benzene solution containing the catalyst, and the subscripts a, b, and t relate respectively to *cyclo*pentadiene, benzoquinone, and to the activated complex. The solubilities of these three molecular species can be represented by

$$\sigma_a = (N_a)^{\mathrm{gas}}(N_a)^{\mathrm{solution}} = \mathrm{e}^{\Delta S_a/\boldsymbol{R}}\mathrm{e}^{-\lambda_a/\boldsymbol{R}T} = C_a\mathrm{e}^{-\lambda_a/\boldsymbol{R}T} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

with precisely analogous expressions for σ_b and σ_t, where ΔS and λ are respectively the entropies and heats of solution. Upon substituting the velocity coefficients and the solubilities in (6) by products of non-exponential and exponential factors [using (2), (7), and the corresponding expressions for σ_b and σ_t], a relationship of the same form as equation (6) in the preceding paper can be obtained. If it is assumed that within a small temperature range the parameters A, E, C, and λ do not measurably alter with temperature and that κ^{n} and κ^{m} in (6) are equal, then it follows that

$$\log A^{\mathrm{m}} - \log A^{\mathrm{n}} = \log C_t^{\mathrm{n}} + \log C_a^{\mathrm{m}} + \log C_b^{\mathrm{m}} - \log C_t^{\mathrm{m}} - \log C_a^{\mathrm{n}} - \log C_b^{\mathrm{n}} \quad . \quad . \quad . \qquad (8)$$

$$E^{\mathrm{m}} - E^{\mathrm{n}} = \lambda_t^{\mathrm{n}} + \lambda_a^{\mathrm{m}} + \lambda_b^{\mathrm{m}} - \lambda_t^{\mathrm{m}} - \lambda_a^{\mathrm{n}} - \lambda_b^{\mathrm{n}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (9)$$

The correlation between the non-exponential and the exponential factors of the solubilities (cf. references in preceding paper) can be written in the following form

$$\log C_a^{\mathrm{m}} - \log C_a^{\mathrm{n}} = r(\lambda_a^{\mathrm{m}} - \lambda_a^{\mathrm{n}}) + q_a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

with analogous expressions for $\log c_b^{\mathrm{m}} - \log c_b^{\mathrm{n}}$ and for $\log c_t^{\mathrm{m}} - \log c_t^{\mathrm{n}}$.

In view of the observations of Evans and Polanyi (see preceding paper), it is assumed that equation (10) and the two analogous expressions with $r \sim 10^{-4}$ cals.$^{-1}$, apply to the participants of such equilibria as (4). The terms on the right-hand side of (10) and its analogues can be substituted, therefore, for those on the right-hand side of (8), leading to

$$\log A^{\mathrm{m}} - \log A^{\mathrm{n}} = r(\lambda_t^{\mathrm{n}} + \lambda_a^{\mathrm{m}} + \lambda_b^{\mathrm{m}} - \lambda_t^{\mathrm{m}} - \lambda_a^{\mathrm{n}} - \lambda_b^{\mathrm{n}}) + (q_a + q_b - q_t) \quad . \quad . \quad . \quad . \quad . \qquad (11)$$

Taking (9) into account, we obtain

$$\log A^{\mathrm{m}} - \log A^{\mathrm{n}} = r(E^{\mathrm{m}} - E^{\mathrm{n}}) + (q_a + q_b - q_t) \quad . \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

which is the suggested functional relationship between the logarithm of the non-exponential A factor of the rate equation (2) and the activation energy.

EXPERIMENTAL.

Benzoquinone, *cyclo*pentadiene, and their addition compound were purified as described in J., 1935, 828. The rate measurements in hexane, carbon disulphide, carbon tetrachloride, nitrobenzene, and acetic acid were carried out in at least two different specimens of each solvent, which was carefully purified by fractional distillation or crystallisation. A measurable change in the reaction velocity could not be observed, and it is concluded that traces of impurities do not produce effects which contribute to the observed solvent influences.

The kinetics of the diene synthesis were measured by using the same colorimetric method as before (*ibid.*). The molar extinction coefficient, η, of benzoquinone and of the addition product were determined in cells the length of which varied from 1 to 20 cm.; Beer's law was found to hold, and there was no measurable change of η with temperature. Numerical values of η in l./g.-mol. cm. are in Table II. The extinction coefficients of the associated molecule in nitrobenzene and acetic acid had to be determined immediately after dissolution, since in these solvents decomposition into the components and subsequent formation of di*cyclo*pentadiene–benzoquinone is much more rapid than in the other solvents. This has to be taken into account in determining the extinction coefficients but not in determining the velocity coefficients, because under the conditions of the kinetic measurements the concentrations are lower.

TABLE II.

Molar extinction coefficients for filter S_{47} *of the Zeiss Stufenphotometer.*

Solvent.	CS_2.	CCl_4.	$PhNO_2$.	$CH_3{\cdot}CO_2H$.	C_6H_{14}.
Benzoquinone	25·5	16·6	16·3	11·5	13·5
*cyclo*Pentadiene–benzoquinone	0·100	0·0700	0·0434	0·0731	0·0809

It has already been stated that those A and E values in Table I which relate to carbon tetrachloride, benzene, and nitrobenzene solution are means of two sets of measurements. The relatively large discrepancies in nitrobenzene solution are possibly due to the fact that this solvent reacts with the product of diene synthesis (1) (cf. Bergmann, *J. Amer. Chem. Soc.*, 1942, **64**, 176), giving rise to the formation of a catalytically active substance, the amount of which would be dependent on concentration or temperature conditions. In carrying out rate measurements in hexane as solvent, it was found that a solution of benzoquinone decomposes in diffuse daylight but not in the light of the photometer lamp. The results of typical rate measurements are in Table III, the second-order velocity coefficients relating to l., g.-mol., and mins.

In each of the solvents referred to in Table III, a number of runs were carried out in which at a given temperature the initial concentration of the reactants was varied. The conclusion that the rate of the formation of *cyclo*pentadiene–benzoquinone can be characterised by second-order velocity coefficients is based on the facts that in individual runs no systematic trend could be observed, and that at various initial concentrations consistent second-order velocity coefficients are obtained which agree within the limits of the experimental error.

TABLE III.

Addition of cyclo*pentadiene to benzoquinone in various solvents. Typical experiments.*

(1) = CS_2; (2) = CCl_4; (3) = $PhNO_2$; (4) = AcOH; (5) = n-C_6H_{14}.
Temp : (1), 3·1°; (2), 40·2°; (3) and (5), 20·4°; (4), 30·0°.
Equimolar initial concns. (g.-mols./l.) : (1), 0·0150; (2), 0·0100; (3), 0·00700; (4), 0·00100; (5), 0·0200.

Expt. (1).			Expt. (2).			Expt. (3).			Expt. (4).			Expt. (5).		
Time, mins.	η, cm.$^{-1}$.	*v.*	Time, mins.	η, cm.$^{-1}$.	*v.*	Time, mins.	η, cm.$^{-1}$.	*v.*	Time, mins.	η, cm.$^{-1}$.	*v.*	Time, mins.	η, cm.$^{-1}$.	*v.*
25	0·363	0·14	6	0·159	0·74	26	0·0993	0·88	18	0·00795	23	42	0·240	0·15
63	0·340	0·12	31	0·136	0·72	41	0·0930	0·87	25	0·00735	22	86	0·217	0·14
91	0·320	0·14	53	0·118	0·78	65	0·0849	0·79	29	0·00688	23	155	0·182	0·16
122	0·305	0·14	113	0·0919	0·73	104	0·0734	0·79	63	0·00445	26	263	0·149	0·16
185	0·287	0·12	185	0·0705	0·75	140	0·0604	0·77	79	0·00386	26	469	0·108	0·16
309	0·238	0·13	—	—	—	200	0·050	0·94	—	—	—	—	—	—
487	0·202	0·12	—	—	—	—	—	—	—	—	—	—	—	—
700	0·165	0·13	—	—	—	—	—	—	—	—	—	—	—	—

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