227. *Kinetics of Bimolecular Associations in Solution and in the Gaseous State. The Mechanism of Additions to Double Bonds. Part IV.*

By ALBERT WASSERMANN.

FOR the further development of the theory of reaction kinetics in the condensed state, it is important to compare the rate of bimolecular reactions in solution and in the gas phase. In this communication experiments are reported from which such a comparison is possible. The diene syntheses, *i.e.*, 1 : 4-additions to conjugated double bonds, now to be discussed, present for the first time reactions between polyatomic molecules which are homogeneous and bimolecular both in the gaseous state and in solution.

Results (cf. *Nature*, 1936, **137**, 497, 707).—The 8 associations of the type $A + B \rightarrow C$, the rates of which will be compared, are collected in Table I, and are numbered for reference. The formulæ are based on the work of Diels and Alder and Alder and Stein [references in Parts I and II (J., 1935, 828, 1511); cf. also Alder, " Handbuch der Biologischen Arbeitsmethoden," Abt. I, Teil II, 2 Hälfte, Bd. II, 1933; Ellis, " The Chemistry of Synthetic Resins," New York, 1935, Chapter 40].

The kinetics of the gaseous reactions 1, 6, 7, and 8 were investigated by Kistiakowsky and Lacher (*J. Amer. Chem. Soc.*, 1936, **58**, 123) by following the pressure change. For the rate measurements in solution (Nos. 1—5) a colorimetric method was used.

The results of the measurements of reaction 1 are in Table II.

The rate constant k was calculated by taking into account all the experiments within this temperature range; E is the activation energy, and A was calculated from k and E according to the Arrhenius equation* $k = Ae^{-E/RT}$. The A values in the last two cols. have been calculated in order to demonstrate the influence of the experimental error : A, max., corresponds to an activation energy 0·5 or 1 kg.-cal. larger, and A, min., to one 0·5 or 1 kg.-cal. smaller than 13·7 or 15·2 kg.-cals.

Table III contains the A and E values for the other diene syntheses of Table I. The accuracy of the activation energies is about 0·6—1 kg.-cal.

In Part I a value of 14·1 ± 1 kg.-cals. was given for the activation energy of reaction 2. The value now reported was determined by using a slightly different technique (cf. Table IV); further, the temperature interval over which the measurements were carried out was larger than before. The A values, both in Part I and in the above table, were calculated according to the Arrhenius equation from $k_{20°}$.

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* In Parts I and II and in *Nature* (*loc. cit.*) the quantity A was designated by Z.

TABLE I.

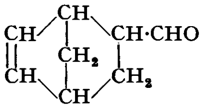
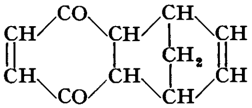
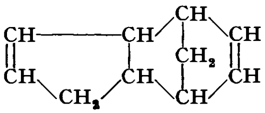
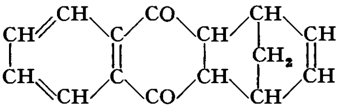
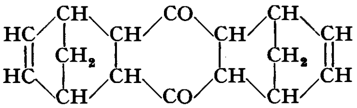
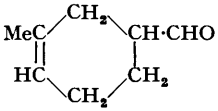
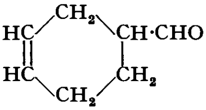
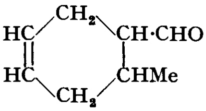
No.	*A* and *B*.	*C*.	Rate measured in :
1	Acraldehyde *cyclo*Pentadiene	 2 : 5-*endo*Methylene-1 : 2 : 5 : 6-tetrahydrobenzaldehyde	Gas phase and benzene solution
2	Benzoquinone *cyclo*Pentadiene	 5 : 8-*endo*Methylene-5 : 8 : 9 : 10-tetrahydro-α-naphthaquinone	Benzene solution
3	*cyclo*Pentadiene (2 mols.)	 4 : 7-*endo*Methylene-4 : 7 : 8 : 9-tetrahydroindene	Benzene solution
4	α-Naphthaquinone *cyclo*Pentadiene	 1 : 4-*endo*Methylene-1 : 4 : 11 : 12-tetrahydroanthraquinone	Benzene solution
5	*cyclo*Pentadiene–benzoquinone *cyclo*Pentadiene	 1 : 4 : 5 : 8-Di*endo*methylene-1 : 4 : 5 : 8 : 11 : 12 : 13 : 14-octahydroanthraquinone	Benzene solution
6	Acraldehyde Isoprene	 2 : 3 : 4 : 5-Tetrahydro-*m*-tolualdehyde	Gas phase
7	Acraldehyde 1 : 3-Butadiene	 1 : 2 : 3 : 6-Tetrahydrobenzaldehyde	Gas phase
8	Crotonaldehyde 1 : 3-Butadiene	 1 : 2 : 3 : 6-Tetrahydro-*o*-tolualdehyde	Gas phase

TABLE II.

Kinetics of the Addition of Acraldehyde to cyclo*Pentadiene.*

	Benzene solution.	Gaseous state.		Benzene solution.	Gaseous state.
Temp. range	5·7—76·5°	107·9—209·8°	$A \times 10^{-6}$, l./g.-mol.-sec.	1·3	1·5
k_r, l./g.-mol.-sec.	$3{\cdot}3 \times 10^{-4}$	$3{\cdot}3 \times 10^{-2}$	$A \times 10^{-6}$, max.	2	5
	(t = 40°)	(t = 160°)	$A \times 10^{-6}$, min.	0·4	0·5
E, kg.-cals.	13·7 ± 0·5	15·2 ± 1			

TABLE III.

Reaction No.	Formulæ of reactants.	$A \times 10^{-6}$ (l./g.-mol.-sec.).	E (kg.-cals.).	
2	$C_6H_4O_2 + C_5H_6$	3·0	11·6	Benzene solution
3	$C_5H_6 + C_5H_6$	1·2	16·4	
4	$C_{10}H_6O_2 + C_5H_6$	0·06	10·0	
5	$C_{11}H_{10}O_2 + C_5H_6$	0·33	13·2	
6	$C_3H_4O + C_5H_8$	1·0	18·7	Gaseous state
7	$C_3H_4O + C_4H_6$	1·5	19·7	
8	$C_4H_6O + C_4H_6$	0·9	22·0	

Discussion.—The kinetic A values in Tables II and III are of the order 10^6 l./g.-mol.-sec. As the bimolecular collision frequency both in the gas phase and in benzene solution is larger by several powers of 10 (cf. below), it follows that only a small fraction of the collisions between the activated molecules is successful.

Diene syntheses are reversible and the " inverse diene syntheses " are unimolecular. The kinetic investigation of the decomposition of *endo*methylenetetrahydrobenzaldehyde in the gaseous state (Kistiakowsky and Lacher, *loc. cit.*), of *endo*methylenetetrahydroindene (di*cyclo*pentadiene) in paraffin solution (Khambata and Wassermann, *Nature*, 1936, **137**, 496), and of *endo*methylenetetrahydro-α-naphthaquinone (*cyclo*pentadiene–benzoquinone) in benzene solution (unpublished experiments) proves that the rate of the inverse diene syntheses 1, 2, and 3 cannot be substantially influenced by a restricted probability of electron transition; for it is found that the kinetic A values amount to 10^{12}—10^{13} sec.$^{-1}$, and such A values are characteristic for " normal " unimolecular reactions (Polanyi and Wigner, *Z. physikal. Chem.*, 1928, **139**, 439; Pelzer and Wigner, *ibid.*, 1932, *B*, **15**, 445). Since the probability of a transition between any two quantum states will be the same for both directions,* it can be concluded that the small A factors of the associations 1, 2, and 3, and probably also those of the other diene syntheses, are not to be explained by rate-restricting transitions, but by the fact that the reactants have a relatively complicated structure (Evans and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 890; cf. also Eyring, *J. Chem. Physics*, 1935, **3**, 107; Hinshelwood and Winkler, this vol., p. 371).

For the comparison of the bimolecular collision frequency in the gaseous and the condensed state, it is useful to regard the A value as a product of a steric factor P and a collision frequency Z, and to define the P value in solution by the P value of the corresponding gas reaction.† Hence we have

$$A_s = P_s \times Z_s;\ A_g = P_g \times Z_g;\ P_s = P_g = P$$

where the subscripts s and g refer to the reaction in solution and in the gas phase respectively.

Bimolecular reactions can be divided into two main types (Moelwyn-Hughes and Hinshelwood, J., 1932, 230; cf. further reference to previous work as quoted by Moelwyn-Hughes, *Chem. Rev.*, 1932, **10**, 241; " Kinetics of Reactions in Solution," Oxford, 1933) :

(1) " Normal " reactions involving simple molecules or simple ions. Here A_s is of the same order as Z_g, *viz.*, 10^{11} l./g.-mol.-sec., and it can be concluded that P is of order unity and Z_s approximately equals Z_g. This conclusion is supported by the fact that the rate of the catalysed conversion of para- into ortho-hydrogen is nearly the same both in the gas phase and in solution (Farkas and Sachse, *Z. physikal. Chem.*, 1933, *B*, **23**, 19).‡

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* See the formulæ given by London, Landau, and Zener (*Z. Physik*, 1932, **74**, 143; *Physikal. Z. Sovietunion*, 1932, **1**, 88; *Proc. Roy. Soc.*, 1932, *A*, **137**, 696).

† Another treatment of collision numbers in solution, involving solubilities (cf. Evans and Polanyi, *loc. cit.*), will be given in a following paper. This treatment is suitable for discussing the previously described change of collision number of a typical diene synthesis in various solvents (cf. *Ber.*, 1933, **66**, 1392).

‡ Previous attempts to measure the rate of bimolecular reactions both in the gaseous and in the condensed state are characterised by two features : (i) when the reaction in the condensed state was bimolecular, the corresponding gas reaction was heterogeneous; (ii) when, however, the reaction was homogeneous in both states, then in one state at least it was not of an ordinary bimolecular type (Moelwyn-Hughes and Hinshelwood, *loc. cit.*; *Proc. Roy. Soc.*, 1931, *A*, **131**, 177; Bowen, Moelwyn-Hughes, and Hinshelwood, *ibid.*, **134**, 211; Beaver and Stieger, *Z. physikal. Chem.*, 1931, *B*, **12**, 93; Bodenstein, Padelt, and Schumacher, *ibid.*, 1929, *B*, **5**, 209; Wulf and Tolman, *J. Amer. Chem.*

(2) " Slow " reactions involving molecules with many internal degrees of freedom. As in the case of diene syntheses, A_s is much smaller than 10^{11} l./g.-mol.-sec. It seems therefore possible *a priori* to assume that here Z_s falls below the gas value.

From the figures in Table III it can be seen that for the gas reactions $P = \sim 10^{-5}$ and that the reactants involved in the diene syntheses in solution are more complex than those involved in the gaseous reactions. As no restricted probability of electron transitions has to be taken into account, it can be concluded that for the reacting molecules here considered, a larger number of internal degrees of freedom will have the effect of either decreasing the steric factor or leaving it unchanged (cf. Evans and Polanyi ; Eyring ; Hinshelwood and Winkler ; *locc. cit.*). Hence it follows that for the reactions in solution the upper limit of P is $\sim 10^{-5}$, and Z_s is not less than 10^{11}. Thus for the slow reactions Nos. 2—4 the collision frequency in benzene solution is not lower than that obtaining in the gas phase.

In the case of reaction 1, A_s equals A_g. It follows that the collision frequency in solution is of the same order of magnitude as that in the gas phase, not only for " normal " bimolecular reactions, but also for a reaction of the " slow " type.

EXPERIMENTAL.

Materials.—The purification of benzoquinone, *cyclo*pentadiene, and *cyclo*pentadiene–benzoquinone was carried out as described in Parts I and II. Acraldehyde (Rhone-Poulenc) was distilled shortly before each experiment in the same apparatus as that used for the purification of *cyclo*pentadiene. α-Naphthaquinone (Schuchardt) was first steam-distilled and then recrystallised successively from alcohol, hexane, carbon disulphide, and ether (charcoal). Di*endo*methyleneoctahydroanthraquinone (di*cyclo*pentadiene–benzoquinone) and *endo*methylenetetrahydroanthraquinone (*cyclo*pentadiene–naphthaquinone) were prepared according to Albrecht (see reference in Part I), and recrystallised from alcohol and hexane respectively. *endo*Methylenetetrahydroindene (di*cyclo*pentadiene) was prepared from the monomeride and purified by distillation in a stream of nitrogen. The products of reactions 2, 4, and 5, as obtained under the conditions of the kinetic measurements, were identified (mixed m. p.) with specimens prepared according to Albrecht.

Colour Measurements.—These were carried out as in Part I (see also *Nature*, 1934, **134**, 101), filter S_{47} being used throughout.

Reaction 2.—All the kinetic measurements, the results of which are collected in Table IX of Part I, were repeated. Practically identical results for the rate constants were obtained in alcoholic and in benzene solution at temperatures of 8·0°, 20·4°, and 25·0°. It was found, however, that the previous values in benzene solution at 29·4° and 40·3° were too large by about 20—30%. This is shown by the data in Table IV and by graph *A* in the figure. The original

TABLE IV.

Addition of Benzoquinone to cyclo*Pentadiene in Benzene Solution.*

Temp. : (*a*) = 34·6°, (*b*) = 50·0°, (*c*) = 50·0°.
Equimolar initial concns. (g.-mol./l.) : (*a*) = 0·00750, (*b*) = 0·00396, (*c*) = 0·00800.
k (l./g.-mol.-min. ; mean value) : (*a*) = 1·0, (*b*) = 2·4, (*c*) = 2·5.

	(*a*).			(*b*).			(*c*).	
t (mins.).	α (cm.$^{-1}$).	*k*.	*t* (mins.).	α (cm.$^{-1}$).	*k*.	*t* (mins.).	α (cm.$^{-1}$).	*k*.
0	0·128	—	0	0·0673	—	0	0·136	—
14	0·115	1·0	15	0·0590	2·4	16	0·104	2·4
42	0·0992	0·9	30	0·0509	2·7	26	0·0879	2·6
68	0·0852	1·0	46	0·0457	2·6	36	0·0773	2·7
95	0·0744	1·0	60	0·0406	2·7	47	0·0723	2·4
175	0·0591	0·9	90	0·0368	2·3	56	0·0643	2·5
∞	0·0005	—	150	0·0301	2·1	61	0·0610	2·5
			248	0·0214	2·2	92	0·0498	2·4
			∞	0·0002	—	∞	0·0004	—

Soc., 1927, **49**, 1650; Rice and Greenberg, *ibid.*, 1934, **56**, 2132; Hinshelwood and Winkler, *Trans. Faraday Soc.*, 1935, **31**, 1739; Daniels, *Chem. Rev.*, 1935, **17**, 82; Thompson, Kearton, and Lamb, J., 1935, 1033). As to the kinetics of the decomposition of ethylene iodide in the two states, see Pollissar, *J. Amer. Chem. Soc.*, 1930, **52**, 956; Schumacher, *ibid.*, p. 3132; Ogg, *ibid.*, 1936, **58**, 607; Arnold and Kistiakowsky, *J. Chem. Physics*, 1933, **1**, 166.

error was connected with the fact that the thickness of the cell was not sufficiently large. Experiment (*a*) in Table IV was carried out as before, except that a cell of greater thickness (4 cm.) was used. In experiment (*b*), 50·0 c.c. of the reaction mixture were added, at the times given in the first column, to about 40 c.c. of benzene at 0°, and diluted to 100 c.c. at room temperature, the colour then being determined in a tube of 15·0 cm. thickness. Experiment (*c*) was carried out like (*b*), but the reaction mixture was diluted to about 4 times the volume before the colour was determined. For the calculation of the rate constants of experiments (*a*) and (*b*), the expansion of the solution between room temperature and 50° had to be taken into account. Here and in those experiments of Table VII, which were carried out above 35° and below 15°, the expansion of the solutions was determined in control experiments.

Reaction 4.—The rate of this reaction was determined by using the same technique as for reaction 2. The molar extinction coefficient of α-naphthaquinone is 9·96 l./g.-mol.-cm. in benzene solution. The validity of Beer's law was proved for the concentration range 0·1—0·007 g.-mol./l. The rate constants were calculated from the equation given in Part I; α_0' is zero since the product of the reaction is colourless.

Typical experiment :

Equimolar initial concn. of α-naphthaquinone and *cyclo*pentadiene = 0·0300 g.-mol./l.; solvent, benzene; temperature, 22·2°.

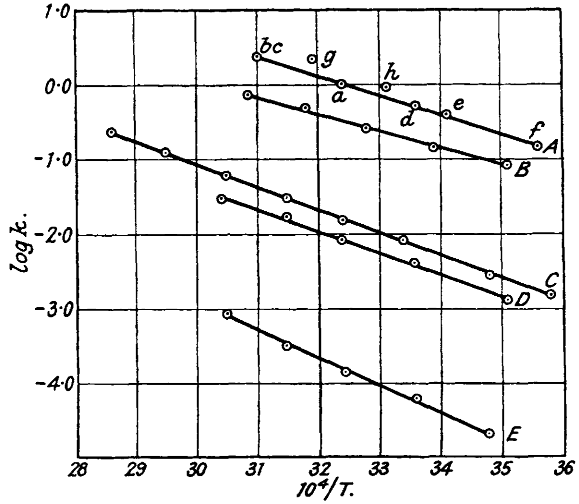
t (mins.)	0	71	95	124	183	273
a (cm.$^{-1}$)	0·299	0·236	0·209	0·195	0·165	0·135
k (l./g.-mol.-min.)	—	0·13	0·15	0·14	0·15	0·15

TABLE V.

Addition of α-Naphthaquinone to cyclo*Pentadiene in Benzene Solution.*

Temp.	Equimolar initial concn. (g.-mol./l.).	$C_{10}H_6O_2$ converted, %.	No. of obstns.	k (mean), l./g.-mol.-min.
11·7°	0·0300	40	4	0·080
22·2	0·0300	53	5	0·14
32·1	0·0300	48	5	0·25
41·5	0·0200	71	7	0·45
51·0	0·0200	71	5	0·70

The E and A values of reactions 2 and 4 were calculated from graphs A and B of the figure.



Temperature Dependence of Rate Constants.

A = Benzoquinone + *cyclo*pentadiene (*a*, *b*, *c*, *d*, *e*, and *f* used for calculation of E and A in Table III; *g* and *h* = measurements at 29·4° and 40·3° in Table IX of Part I).
B = α-Naphthaquinone + *cyclo*pentadiene. C = Acraldehyde + *cyclo*pentadiene.
D = *cyclo*Pentadiene-benzoquinone + *cyclo*pentadiene. E = *cyclo*Pentadiene + *cyclo*pentadiene.

Colorimetric Determination of cyclo*Pentadiene.*—A known quantity of *cyclo*pentadiene was added to an excess of solid benzoquinone, and after some days the benzoquinone still present was determined colorimetrically. From the amount of benzoquinone converted, the concentration of *cyclo*pentadiene at the moment of mixing can be calculated. This analytical method was tested by 10 experiments in which the concentration as determined by weighing was compared with that determined colorimetrically. The solvent used was benzene, and the temperature of the solution at the moment of mixing with benzoquinone was 20° or 75°. A number of added substances, *e.g.*, *cyclo*pentadiene–benzoquinone, di*cyclo*pentadiene, or acraldehyde, did not influence the accuracy of this method, which is 3—5% if the colour is determined as indicated on p. 1031.

Reactions 1, 3, *and* 5.—The joints of the measuring flasks used for the following experiments were sealed with mercury in order to avoid evaporation. At known time intervals, a measured amount of the reaction mixture was added to an excess of solid benzoquinone. The *cyclo*pentadiene concentration at the moment of mixing can be calculated as indicated above, because at room temperature the rate constant of the *cyclo*pentadiene–benzoquinone reaction is, at least, 100 times as great as the rate constant to be determined. The rate constants as given in the following tables were calculated by using the ordinary integrated equation for bimolecular reactions. Under the conditions of the kinetic measurements, the rate of the back reaction and that of side reactions is so slow that the use of the simple formula is justified.

Table VI contains the data of three typical experiments. The *cyclo*pentadiene concentration in col. 7 corresponds to the time given in col. 1. The volumes of solution given in col. 2 were added to solid benzoquinone in a measuring flask the volume of which is given in col. 4. Before the penetrability (col. 6) was determined, the mixture was made up to the mark and then diluted as many times as shown by the figures in col. 5. For the colour measurements a cell of 1 cm. thickness was used. The accuracy of the k values in col. 8 is about 8%.

TABLE VI.

Diene Syntheses Nos. 1, 3, *and* 5 *in Benzene Solution : Typical Experiments.*

Equimolar initial concns. (g.-mol./l.) : (1) = 0·200; (3) = 1·358; (5) = 0·274.
Temp. : (1) = 45·0°; (3) = 25·1°; (5) = 11·9°.

	Time, mins.	Vol. of solution (20°) used, c.c.	Benzoquinone, g.	Vol. of measuring flask.	Number of times diluted.	Penetrability, %.	Concn. of C_5H_6 (g.-mol./l.).	10^3k (l./g.-mol.-min.).
(1)	76	4·90	0·2055	10·0	5·00	38·5	0·139	29
	133	4·90	0·1942	10·0	5·00	38·2	0·116	27
	245	4·90	0·1899	10·0	5·00	35·1	0·0855	27
	395	4·90	0·2238	25·0	3·33	43·4	0·0546	27
	543	4·90	0·1857	25·0	2·00	31·2	0·0471	30
	710	4·90	0·1520	25·0	0	15·0	0·0398	28
(3)	1,600	0·900	0·1365	10·0	0	44·8	1·177	0·070
	2,910	0·900	0·1483	10·0	1·67	38·9	1·077	0·066
	4,650	0·900	0·1460	10·0	1·67	32·5	0·977	0·062
	9,060	0·900	0·1730	10·0	5·00	49·9	0·792	0·059
	14,370	0·900	0·1404	25·0	1·67	49·6	0·617	0·061
	21,460	0·900	0·1336	25·0	1·67	46·6	0·470	0·065
(5)	190	5·00	0·1777	10·0	1·67	32·2	0·232	1·3
	352	4·00	0·1440	10·0	1·67	33·9	0·218	1·5
	680	4·00	0·1402	10·0	2·00	39·0	0·204	1·3
	1,460	4·00	0·1287	10·0	2·00	36·6	0·170	1·3
	2,830	4·00	0·1207	10·0	2·00	32·8	0·137	1·2
	4,320	4·00	0·1017	10·0	1·43	25·2	0·109	1·2

The graphs *C*, *D*, *E* in the figure were used for the calculation of the *A* and *E* values given in Tables II and III.

SUMMARY.

(1) The kinetics of five diene syntheses are measured in benzene solution and compared with those of five similar syntheses in the gas phase as investigated by Kistiakowsky and Lacher.

(2) The " temperature-independent " factor of the Arrhenius equation of the diene syntheses is much smaller than the collision frequency in the gas phase. For reactions 1, 2, and 3, and probably also for the other reactions, this is not connected with a restricted probability of electron transitions, but with the complicated structure of the reactants.

(3) The collision frequency in solution can be of the same order of magnitude as that

TABLE VII.

Diene Syntheses Nos. 1, 3, *and* 5. *Results of Kinetic Measurements.*

	Temp.	Equimolar initial concn. (g.-mol./l.).	C_5H_6 converted, %.	No. of obstns.	10^3k (mean).
(1)	5·7°	0·400	75	4	1·5
	14·8	0·200	80	5	2·7
	25·2	0·200	80	5	7·4
	25·2	0·400 *	80	5	8·0
	35·0	0·200	82	4	15
	45·0	0·200	80	6	28
	55·1	0·200	75	6	57
	65·2	0·100	71	5	120
	76·5	0·100	76	5	220
(3)	15·1°	1·488	53	5	0·023
	25·1	1·358	71	5	0·062
	25·0	2·000	53	5	0·059
	35·0	1·410	63	6	0·14
	45·0	1·052	70	6	0·32
	55·2	1·118	92	6	0·82
(5)	11·9	0·247	56	6	1·3
	25·0	0·203 †	79	5	4·0
	35·0	0·223	83	7	7·9
	45·1	0·265	88	6	17
	55·4	0·206	77	6	27

* Reaction mixture at zero time = 36·5 c.c.; 0·5 g. glass wool was added.

† This concentration corresponds to *cyclo*pentadiene–benzoquinone; the initial concentration of *cyclo*pentadiene was 0·172 g.-mol./l.

obtaining in the gas phase, not only for "normal" bimolecular reactions, but also for a reaction of the "slow" type.

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UNIVERSITY COLLEGE, LONDON, W.C. 1.

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